U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-268 029

Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations

Municipal Environmental Research Lab, Cincinnati, Ohio

May 77

PB 268 029

Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U. S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
WATER SUPPLY RESEARCH DIVISION

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/8-77-005		

4. TITLE AND SUBTITLE	5. REPORT DATE
Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations	May 1977 (Issuing Date) 6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas J. Sorg, O. Thomas Love, Jr., Gary S. Logsdon	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Water Supply Research Division Municipal Environmental Research Laboratory 26 W. St. Clair Street Cincinnati, Ohio 45268	1CC614 11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory--Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Contact: T. Sorg, (8-684-7228) Cincinnati, OH

16. ABSTRACT

Following the passage on December 16, 1974, of Public Law 93-523, The Safe Drinking Water Act, the Interim Primary Drinking Water Regulations were promulgated on December 24, 1975, to take effect June 24, 1977. These regulations set Maximum Contaminant Levels (MCL) for ten inorganic constituents, turbidity, coliform organisms, six pesticides and radionuclides.

PL-93-523 stated that the Primary Drinking Water Regulations should consist of MCLs as well as a statement of treatment technology that could be used to achieve these levels. This document provides that information. It contains five sections as related to the five groups of Interim Primary Drinking Water Regulations noted above. This document, based on the literature and the research being conducted by the Water Supply Research Division, is not meant to stifle innovative treatment technology. It attempts to be a statement of technology known at the time of the effective date of the Interim Primary Drinking Water Regulations that will allow utilities, with assistance from their consulting engineers, to apply whatever treatment might be necessary to improve their drinking water quality such that it meets the Interim Primary Drinking Water Regulations.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Water Treatment Water Purification Chlorination Coagulation Filtration Chemical Removal (Water Treatment) Potable Water Ion Exchanging Microorganism Control (Water) Absorption	Interim Primary Drinking Water Regulations Public Law 93-523	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	80
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	PC A05 - A01

EPA Form 2220-1 (9-73)

EPA-600/8-77-005

Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations

U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
MUNICIPAL ENVIRONMENTAL RESEARCH LABORATORY
WATER SUPPLY RESEARCH DIVISION
Cincinnati, Ohio
May 1977

1a

NOTICE. The mention of trade names of commercial products in this publication is for illustration purposes, and does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

Contents

Page

Introduction 1

Treatment Techniques for the Removal of Inorganic Contaminants from Drinking Water 2
- Arsenic (As) 7
  - As^{+5} Removal 7
  - As^{+3} Removal 7
  - Arsenic Removal (General) 10
  - References 10
- Barium (Ba) 11
  - Removal 11
  - References 11
- Cadmium (Cd) 13
  - Removal 13
  - References 14
- Chromium (Cr) 16
  - Cr^{+3} Removal 16
  - Cr^{+6} Removal 17
  - References 18
- Fluoride (F) 20
  - Removal 20
  - References 21
- Lead (Pb) 21
  - Removal 21
  - References 21
- Mercury (Hg) 24
  - Inorganic Mercury Removal 24
  - Organic Mercury Removal 24
  - References 25

Nitrate (NO_3) 28
Removal 28
References 29
Selenium (Se) 29
Se^{+4} Removal 29
Se^{+6} Removal 29
References 30
Silver (Ag) 32
Removal 32
References 32
Treatment Costs for the Removal of Inorganic Contaminants 34
Cost of Modifications or Operational Changes at Existing Treatment Plants 34
Cost of New Treatment Facilities 34
References 36

Treatment Techniques for the Removal of Turbidity from Drinking Water 37
Treatment Techniques 37
Granular Media Filtration 38
Diatomaceous Earth Filtration 38
Disposal of Filter Plant Sludge 39
Treatment Costs for Turbidity Removal 39
References 40

Treatment Techniques for the Removal of Coliform Organisms from Drinking Water 44
Maximum Contaminant Levels (MCL's) 44
Disinfection of Water 45
Turbidity 45
Disinfection Byproducts 45
Chlorination 45
Ozone 45
Chlorine Dioxide 50
Cost of Water Disinfection 51
Summary 51
References 52

Treatment Techniques for the Removal of Organic Contaminants from Drinking Water 53
Occurrence of Pesticides in Water Supplies 53
Endrin 53
Lindane 54
Toxaphene 55
2,4-D 55
2,4,5-TP (Silvex) 56
Methoxychlor 56
Summary of Treatment Techniques 56
Estimating Cost for Reducing Trace Organics (Pesticides) Below MCL 59
Adsorption With PAC 59
Adsorption With GAC 59
References 59
Bibliography—Occurrence and Fate of Pesticides in the Environment 61

Treatment Techniques for the Removal of Radioactive Contaminants from Drinking Water 62
Alpha Emitters 62
Maximum Contaminant Levels 62
Radium in Water Supplies 63
Removal of Radium from Water 63
Lime or Lime-Soda Softening 63
Ion Exchange Softening 63
Reverse Osmosis 63
Disposal of Treatment Water 65
Methods for Lime Sludge Disposal 65
Methods for Lime Softening Backwash Disposal 66
Ion Exchange Brine Disposal 66
Disposal of Reverse Osmosis Wastes 66
Treatment and Disposal Costs to Remove Alpha Emitters 67
Manmade Radionuclides, or Beta and Photon Emitters 67
Maximum Contaminant Levels 67
Monitoring for Beta and Photon Emitters 71
Removal of Manmade Radioactivity 71
Glossary 72
References 72

Introduction

Following the passage on December 16, 1974, of Public Law 93-523, the Safe Drinking Water Act, the National Interim Primary Drinking Water Regulations were promulgated on December 24, 1975, to take effect June 24, 1977. These regulations set maximum contaminant levels (MCL's) for 1) 10 inorganic constituents, 2) turbidity, 3) coliform organisms, 4) 6 pesticides, and 5) radionuclides.

Public Law 93-523 stated that the Primary Drinking Water Regulations should consist of MCL's and identify treatment technology that could be used to achieve them. This document provides the latter information in five sections as related to the foregoing five groups of Interim Primary Drinking Water Regulations. It is based on the literature and the research being conducted by the Water Supply Research Division, and is not meant to stifle innovative treatment technology. It attempts to state technology known at the date of effectiveness of the Interim Primary Drinking Water Regulations that will allow utilities, with assistance from their consulting engineers, to apply whatever treatment might be necessary to improve their drinking water quality such that it meets the Interim Primary Drinking Water Regulations.

One difficulty encountered in preparing this document was the lack of information on treatment technology applicable to the small water utilities serving 1,000 consumers or less. Research is now underway in an attempt to fill that void; because the research has not been completed, this document does not contain the information. Cost data were another difficulty. It is impossible to prepare treatment cost information that is universally applicable to all utilities. The authors, therefore, recognize that the costs contained in this document may not apply to all situations.

The authors hope that this document will be helpful to consulting engineers and to water utilities. They anticipate, however, that it will need to be updated as new information on treatment technology becomes available through research and development and experience at the many treatment plants now in operation.

A list of references concerning each contaminant follows the relevant discussion.

Treatment Techniques for the Removal of Inorganic Contaminants from Drinking Water

by THOMAS J. SORG
Water Supply Research Laboratory, MERL
U.S. Environmental Protection Agency
Cincinnati, Ohio

The National Interim Primary Drinking Water Regulations established maximum contaminant levels (MCL's) for 10 inorganic chemicals: arsenic, barium, cadmium, chromium, fluoride, lead, mercury, nitrate, selenium, and silver (tables 1 and 2). Except for nitrate, the MCL's for all of these inorganic chemicals are applicable to community water supply systems. The nitrate level applies to both community and noncommunity systems.[1]

Most of the treatment information and data available for the removal of inorganic chemicals are on conventional coagulation or lime softening treatment. These treatment methods are commonly used by large water supplies. As stated in the Introduction, research is underway to fill the need for information on treatment technology applicable to small water systems.

There have been many studies on the removal of some of the inorganic contaminants from municipal and industrial wastewater, but few have been conducted on the removal of these contaminants from drinking water sources that would generally contain much lower concentrations. A review of the literature indicates that much of the available information on drinking water is the result of laboratory and pilot plant studies conducted by the Water Supply Research Division, U.S. Environmental Protection Agency, in Cincinnati, Ohio. The EPA research program centered on conventional coagulation and lime softening treatment methods. Only when these methods were found to be ineffective were other methods studied, such as reverse osmosis and ion exchange.

The studies by EPA and others have shown that no one treatment technique is effective for all contaminants. A summary of the best treatment methods for the inorganic contaminants is presented in table 3. Most of the methods listed are conventional coagulation and lime softening. Other treatment techniques—such as ion exchange, reverse osmosis, distillation, and electrodialysis—may be equally effective. These methods are generally more expensive and, except for ion exchange, they are not commonly used for treating drinking water. They may have practical applications in special cases, however, particularly for small communities, and should not be ruled out entirely. Because data are lacking on their effectiveness to remove certain contaminants from drinking water, these systems are not discussed in detail.

The studies on conventional coagulation treatment and lime softening showed that removal results frequently depend on the pH of the treated water, the type and dose of the coagulant, and initial concentration of the contaminant. Of these variables, the most important was found to be the pH of the treated water (figs. 1, 2, and 3). This finding is logical because the solubility limits for metal hydroxides, carbonates, and so forth, are normally pH dependent.

Another important factor in the removal of a contaminant is its valence. Several contaminants, such as arsenic, chromium, and selenium, may be found in water in more than one valence state. Mercury may be found in either the organic or inorganic form. Studies of these substances have shown significant differences in removals between forms of the contaminants. For example, the oxidized state of arsenic (As^{+5}) is easily removed by conventional coagulation treatment, whereas the reduced state (As^{+3}) is not (figs. 1, 2, and 3). The valence of the contaminant is an important consideration, therefore, in selecting the proper treatment technique.

[1] See National Interim Primary Drinking Water Regulations for definitions of community and noncommunity systems.

TABLE 1. National Interim Primary Drinking Water Regulations: Maximum Contaminant Levels (MCL's) for Inorganic Contaminants Except Fluoride[a]

Contaminant	MCL, mg/l
Arsenic	0.05
Barium	1.
Cadmium	0.010
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10
Selenium	0.01
Silver	0.05

[a]The MCL for fluoride is determined by the annual average of the maximum daily air temperature for the location in which the community water system is situated (see table 2).

TABLE 2. National Interim Primary Drinking Water Regulations: Maximum Contaminant Level (MCL)[a] for Fluoride

Temperature		MCL, mg/l
°F	°C	
53.7 and below	12.0 and below	2.4
53.8 to 58.3	12.1 to 14.6	2.2
58.4 to 63.8	14.7 to 17.6	2.0
63.9 to 70.6	17.7 to 21.4	1.8
70.7 to 79.2	21.5 to 26.2	1.6
79.2 to 90.5	26.3 to 32.5	1.4

[a]Determined by the annual average of the maximum daily air temperature for the location in which the community water system is situated.

TABLE 3. Most Effective Treatment Methods for Inorganic Contaminant Removal

Contaminant	Most effective methods
Arsenic:	
As^{+3}	Ferric sulfate coagulation, pH 6-8
	Alum coagulation, pH 6-7
	Excess lime softening
	Oxidation before treatment required
As^{+5}	Ferric sulfate coagulation, pH 6-8
	Alum coagulation, pH 6-7
	Excess lime softening
Barium	Lime softening, pH 10-11
	Ion exchange
Cd^{+3}	Ferric sulfate coagulation, above pH 8
	Lime softening
	Excess lime softening
Chromium:	
Cr^{+3}	Ferric sulfate coagulation, pH 6-9
	Alum coagulation, pH 7-9
	Excess lime softening
Cr^{+6}	Ferrous sulfate coagulation, pH 7-9.5
Fluoride	Ion exchange with activated alumina or bone char media
Lead	Ferric sulfate coagulation, pH 6-9
	Alum coagulation, pH 6-9
	Lime softening
	Excess lime softening
Mercury:	
Inorganic	Ferric sulfate coagulation, pH 7-8
Organic	Granular activated carbon
Nitrate	Ion exchange
Selenium:	
Se^{+4}	Ferric sulfate coagulation, pH 6-7
	Ion exchange
	Reverse osmosis
Se^{+6}	Ion exchange
	Reverse osmosis
Silver	Ferric sulfate coagulation, pH 7-9
	Alum coagulation, pH 6-8
	Lime softening
	Excess lime softening

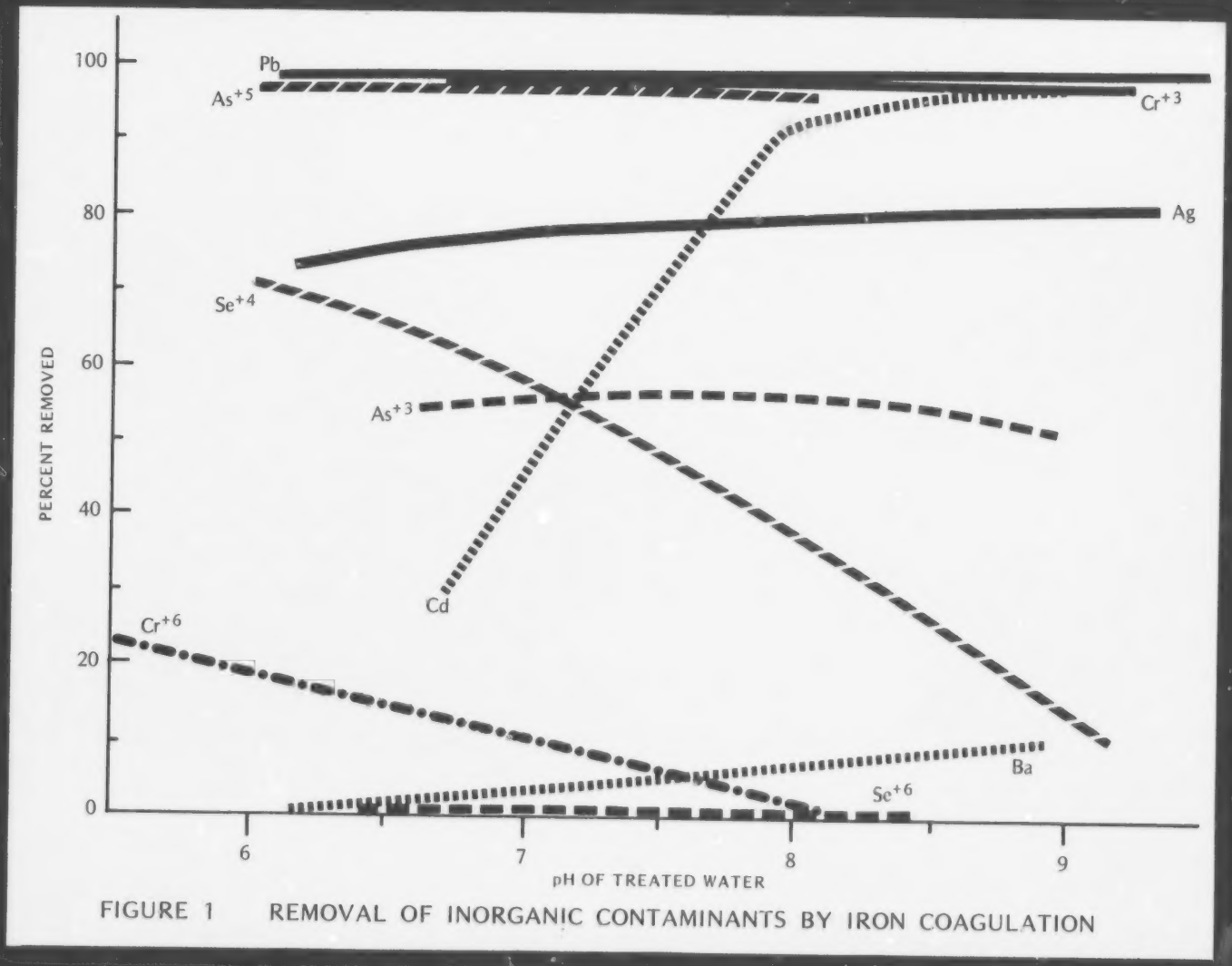


FIGURE 1 REMOVAL OF INORGANIC CONTAMINANTS BY IRON COAGULATION

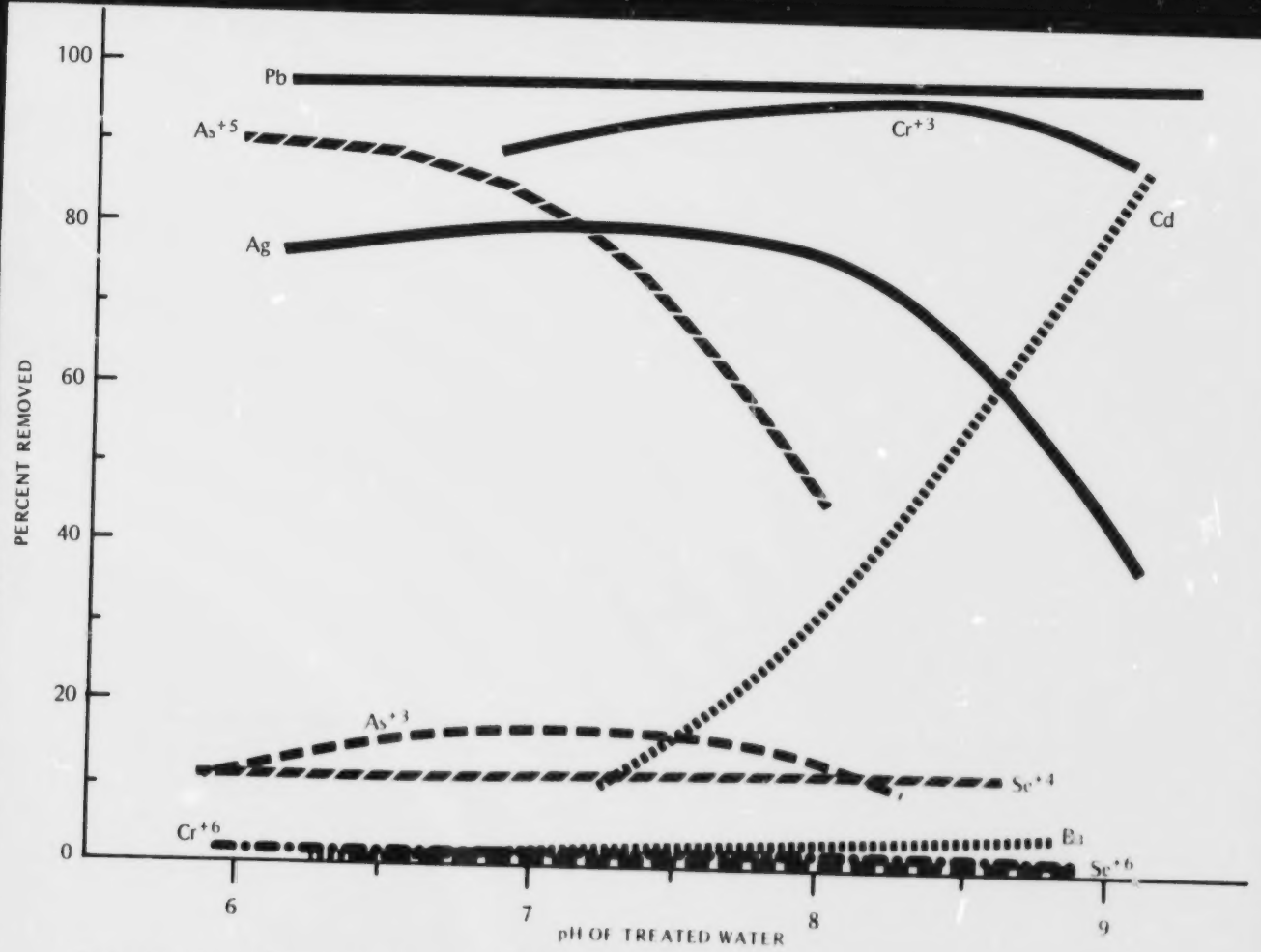


FIGURE 2 REMOVAL OF INORGANIC CONTAMINANTS BY ALUM COAGULATION

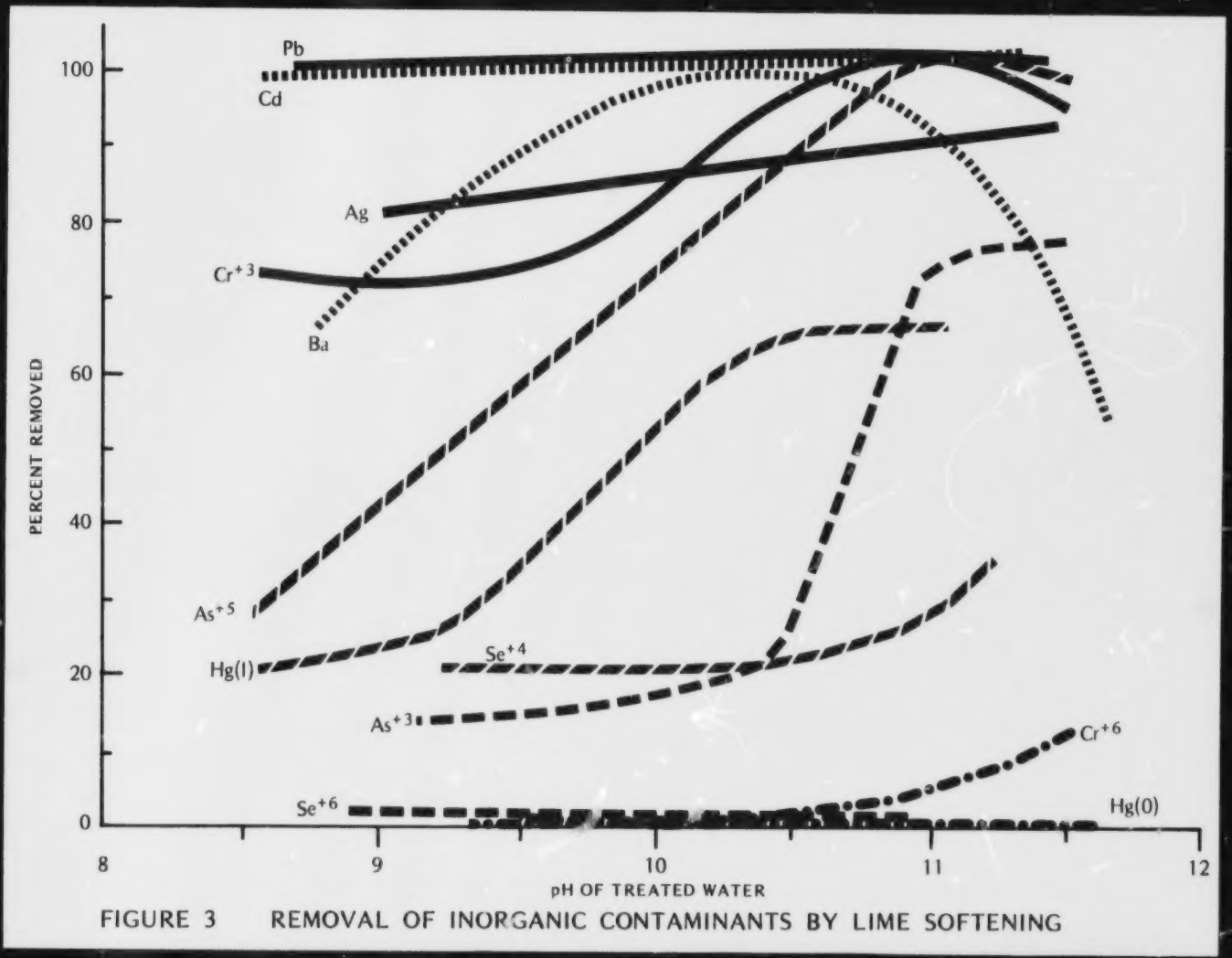


FIGURE 3 REMOVAL OF INORGANIC CONTAMINANTS BY LIME SOFTENING

Standard analytical detection methods (atomic adsorption) do not distinguish between valence states, but measure only the total concentration. Such measurements are adequate for normal routine monitoring, but if treatment must be provided to lower the concentration, additional analytical testing is recommended to identify the form of the contaminant to determine the proper treatment method.

Information on the chemistry and occurrence of inorganic substances in water indicates that normally the reduced form of a contaminant is found in ground water, and the oxidized form in surface water. Furthermore, the more naturally occurring substances are generally found in ground water, and those occurring from industrial pollution are usually found in surface waters. This type of information is also useful and can serve as a guide in selecting the proper treatment technique. The form, however, may change because of the oxidation-reduction conditions of the water; therefore, it is advisable to identify the form of the contaminant and routinely check it during treatment.

Arsenic (As)

MCL: 0.05 mg/l
Common Valence Forms:
+3 (arsenite)
+5 (arsenate)
Most Likely Occurrence and Source of Contaminant:
+3 Ground water—natural occurrence
+5 Ground water—natural occurrence
Surface water—natural occurrence or industrial pollutant

The standard analytical procedures used to determine the amount of arsenic in water measure only total arsenic and do not distinguish between the two valence forms. Because of significant differences in removals of each form by conventional coagulation and lime softening treatment methods, the arsenic form should be determined before selecting a treatment method or modifying an existing facility. Furthermore, the treatment modification or design should take into account the potential valence change of the arsenic before treatment caused by the oxidation-reduction characteristics of the raw water.

It is not as important to identify the valence of arsenic if the treatment technique selected is either ion exchange or reverse osmosis. The literature indicates, however, that arsenic should be found in the anion form in aqueous solutions as either AsO_2^{-1} or AsO_4^{-3} and therefore, the selection of the type of ion exchange resin is significant (1).

As^{+5} REMOVAL

Laboratory experiments and pilot plant studies on specific forms of arsenic have shown that As^{+5} can be removed from water very effectively by conventional alum or iron coagulation and by lime softening treatment processes (2-5). These studies, however, demonstrated that arsenic removals depend on the pH of the treated water, the coagulant dose, and the initial arsenic concentration, with pH being the most important factor (figs. 4 through 7).

Alum and ferric sulfate coagulation (20-30 mg/l) achieved over 90 percent removal of As^{+5} (0.3 mg/l) between pH 5.0 and 7.5. Above pH 7.5, As^{+5} removals decreased, particularly with alum coagulation. When the initial concentration was increased above 1.0 mg/l, arsenic removals decreased as the concentration increased, particularly with alum coagulation. Larger doses of coagulant, however, produced higher removals and might be necessary to achieve the MCL.

Lime softening was also found very effective for As^{+5} removal. At pH 10.8 and above, 95 percent removals were achieved with raw water concentration of 0.1 to 10.0 mg/l. Below pH 10.8, removals decreased as the pH decreased, to about 30 percent at pH 8.5 (3).

As^{+3} REMOVAL

Laboratory and pilot plant experiments have shown that As^{+3} is not removed as effectively from water as As^{+5} either by iron or alum coagulation or by lime softening treatment processes (figs. 4 through 7). In the pH range of 5.5-9.0, alum coagulation (30 mg/l) removed less than 20 percent and ferric sulfate (30 mg/l) 60 percent or less of 0.3 mg/l of As^{+3}. Furthermore, As^{+3} removals decreased with increasing concentrations. Lime softening was shown to be only slightly more effective, removing about 70 percent of 0.3 mg/l of As^{+3} at pH 10.8 and above. Below this pH, removals decreased to less than 20 percent (3).

As^{+3} can be removed from water by conventional coagulation and lime softening by oxidizing it to As^{+5} before treatment. Laboratory studies have demonstrated that the conventional chlorination disinfection process before treatment will result in As^{+3} removals similar to those achieved on As^{+5} by the

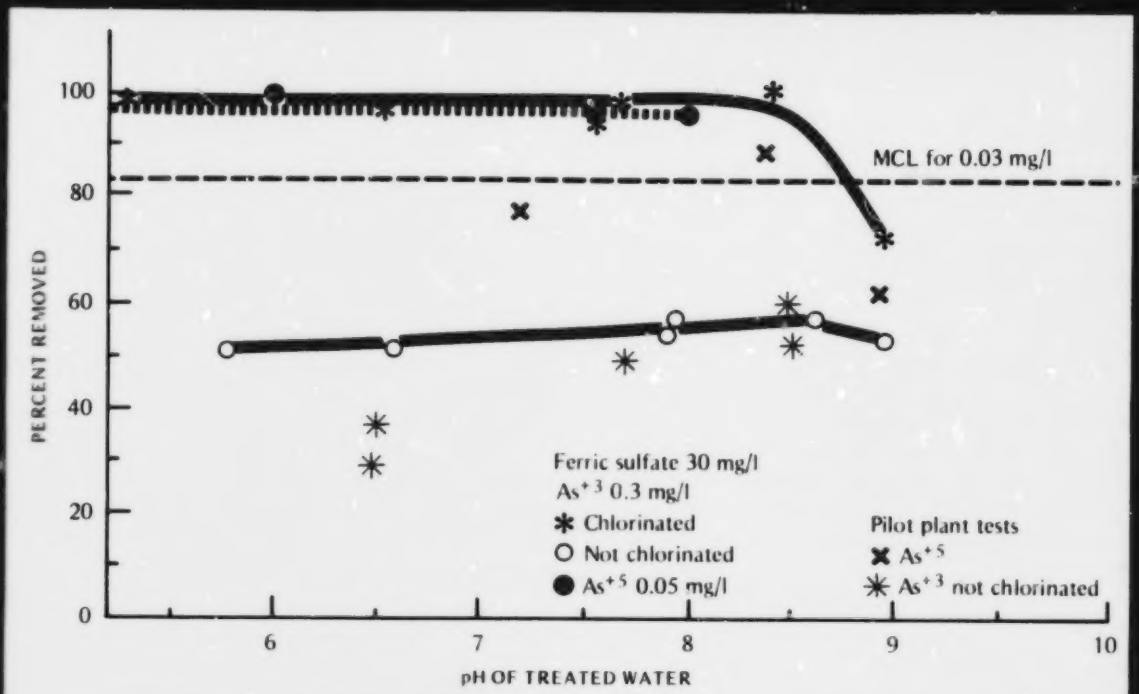


FIGURE 4 ARSENIC REMOVAL BY IRON COAGULATION (2,3)

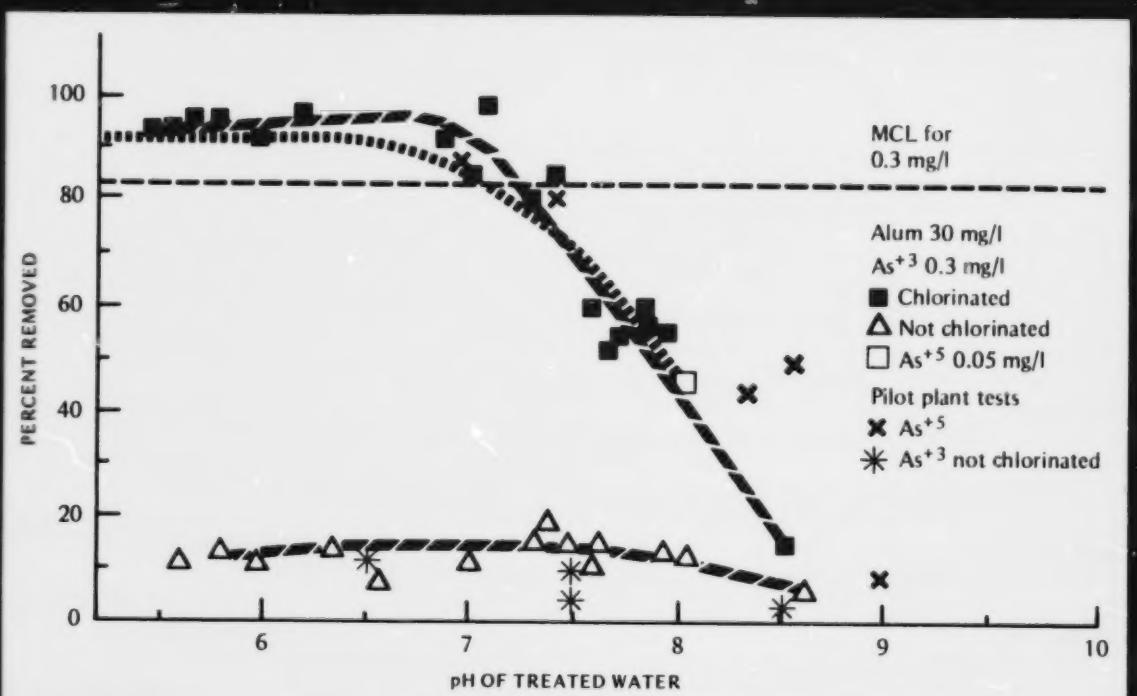


FIGURE 5 ARSENIC REMOVAL BY ALUM COAGULATION (2,3)

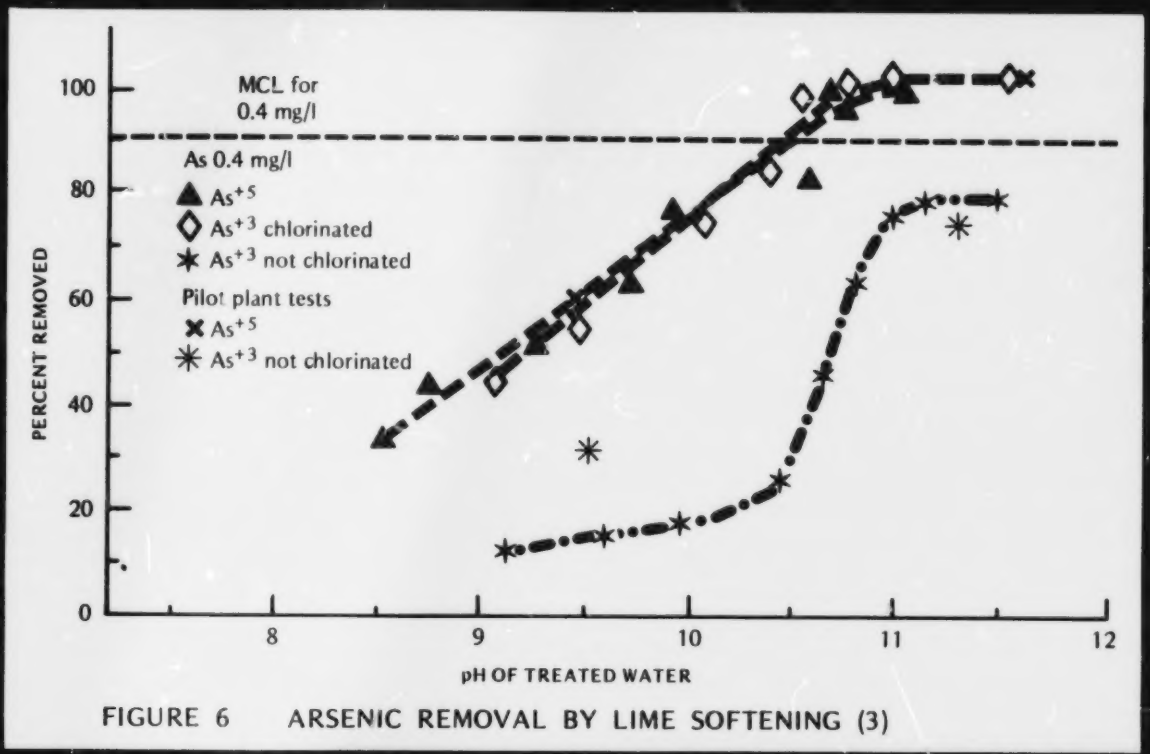


FIGURE 6 ARSENIC REMOVAL BY LIME SOFTENING (3)

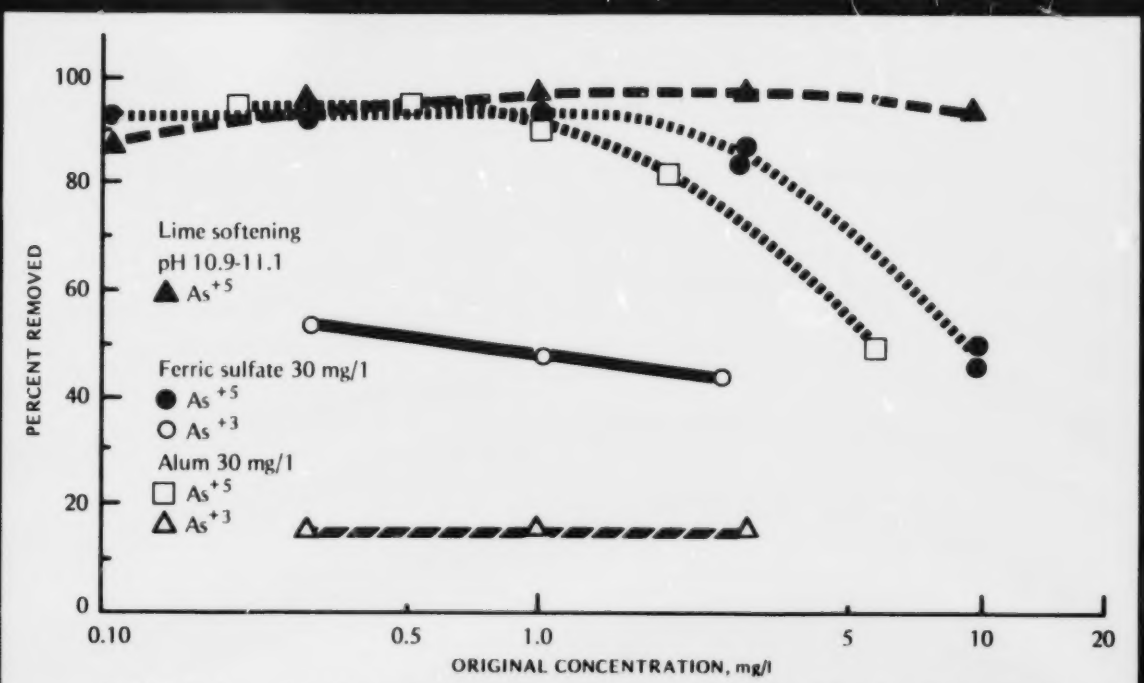


FIGURE 7 ARSENIC REMOVAL BY COAGULATION AND LIME SOFTENING (3)

same treatment processes (3). And studies have shown that potassium permanganate should also be an effective oxidant (6).

Recent investigations have found that the reaction of chlorine with certain organic materials produces chloroform and other related organic byproducts. Consequently, the use of chlorine as an oxidant for As^{+3} removal may not be advisable.

ARSENIC REMOVAL (GENERAL)

Laboratory and pilot plant studies and full-scale treatment for arsenic removal have been conducted in Taiwan on ground water and synthetic waters (6). The valence form of arsenic was not identified in the ground water, but the removal results by the various treatment techniques studied suggest As^{+3}. Laboratory and pilot plant study results showed that the best removals, nearly 100 percent, were achieved with iron coagulation when the raw water was oxidized before treatment. Both chlorine and potassium permanganate were used as oxidants with about equal success. Aeration was not effective.

Based upon the laboratory and field experiments, a full-scale iron coagulation water plant was built in 1969 to serve 1,500 people in Taiwan. Arsenic removal data over a 4-month period showed the raw water to contain 0.36-0.56 mg/l of arsenic and the treated water to be free of arsenic. The pH of the finished water ranged from 7.7 to 8.3.

A few laboratory studies have been conducted on the removal of arsenic by ion exchange (7,8). Cation exchangers, both of the H and Na form, produced no removal. Several different anion exchange resins have been tested and found to remove from 55 to 100 percent of the arsenic. This work confirms that arsenic is found as an anion in water and that an anion exchange resin is required to remove arsenic.

Activated alumina has also been found to remove arsenic from water (9). Experiments on synthetic water and a ground water containing arsenic showed activated alumina to lower the arsenic content from 0.05-0.1 mg/l to 0.01 mg/l or less. No pilot plant or full-scale treatment data are available.

REFERENCES

1. O'Connor, J. T. Removal of Trace Inorganic Constituents by Conventional Water Treatment Processes. In: *Proceedings of the 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71 (108):99-110, 1974.
2. Gulledge, J. H., and J. T. O'Connor. Removal of As(V) from Water by Adsorption on Aluminum and Ferric Hydroxide. *J. Am. Water Works Assoc.*, *65*(8):548-554, 1973.
3. Logsdon, G. S., T. J. Sorg, and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71, 1974. Pp. 111-133.
4. Logsdon, G. S., and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of a Symposium on Trace Metals in Water Removal Processes and Monitoring.* U.S. Environmental Protection Agency, New York, N.Y., 1973. Pp. 225-256.
5. Logsdon, G. S., and J. M. Symons. Removal of Trace Inorganics by Drinking Water Treatment Unit Processes. *AICE Symp. Ser.*, *70*(136):367-377, 1974.
6. Shen, Y. S. Study of Arsenic Removal from Drinking Water. *J. Am. Water Works Assoc.*, *65*(8):543-548, 1973.
7. Calmon, C. Comments. *J. Am. Water Works Assoc.*, *65*(8):586-589, 1973.
8. Calmon, C. Removal Processes by Ion Exchange. In: *Proceedings of Symposium of Traces of Heavy Metals in Water Removal Processes and Monitoring.* U.S. Environmental Protection Agency, New York, N.Y., 1973, Pp 7-42.
9. Bellack, E. Arsenic Removal from Potable Water. *J. Am. Water Works Assoc.*, *63*(7):454-458, 1971.

Barium (Ba)

MCL: 1.0 mg/l
Common Valence Form: +2
Most Likely Occurrence and Source of Contaminant:
Ground water—natural occurrence

REMOVAL

Laboratory studies have been conducted on the removal of barium from ground water by iron and alum coagulation and lime softening (1-3). Lime softening achieved greater than 90 percent removal in the 10-11 pH range on well water containing 7-8.5 mg/l of naturally occurring barium (fig. 8). Removals decreased below and above this range.

Pilot plant studies and full-scale treatment information on similar types of ground water verified the laboratory data (4). Pilot plant test runs on water containing 10-12 mg/l of barium at pH 9.2, 10.5, and 11.6 resulted in removals of 84, 93, and 82 percent, respectively. Grab samples from two full-scale lime softening plants showed removals of 88 and 95 percent. These plants operated at pH 10.5 and 10.3, and the raw water barium concentrations were measured at 7.5 and 17.4 mg/l, respectively (4).

Alum and ferric sulfate coagulation were not effective for barium removal. Laboratory tests showed that alum coagulation could achieve only about 20 percent removal even when using 120 mg/l of alum (figs. 9 and 10). Ferric sulfate coagulation was only slightly better than alum, achieving 35 percent removal with 120 mg/l of coagulant (figs. 9 and 10). Conventional coagulation, therefore, is not considered a good method for barium removal, unless the barium concentration is only slightiy above the MCL.

An alternative treatment method to lime softening for barium removal is ion exchange. Field data from two midwestern full-scale ion exchange softening plants showed that barium removal was comparable to hardness removal on well water containing 11-19 mg/l of barium and 225-230 mg/l of hardness as $CaCO_3$ (4). When these softening units were performing efficiently and removing all of the hardness from the water, they also removed all of the barium. Furthermore, barium breakthrough occurred at about the same time as hardness breakthrough. As a result of the similarity in behavior of hardness and barium in ion exchange treatment, the hardness test can be used as a practical method to monitor barium during treatment.

Although ion exchange softening treatment may be very effective for barium removal, this technique may not always be practical on waters containing very high barium concentrations. In normal softening treatment, raw water is blended with the treated water to lower treatment costs and to provide a finished water with a reasonable amount of hardness. If the barium concentration is high, blending may not be possible to maintain the barium concentration in the finished water below the MCL. Furthermore, hardness would also have to be added to the very soft treated water, which would result in higher than normal treatment cost.

REFERENCES

1. Logsdon, G. S., T. J. Sorg, and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71, 1974. Pp. 111-113.
2. Logsdon, G. S., and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of a Symposium on Trace Metals in Water Removal Processes and Monitoring.* U.S. Environmental Protection Agency, New York, NY., 1973. Pp. 225-256.
3. Logsdon, G. S., and J. M. Symons. Removal of Trace Inorganics by Drinking Water Treatment Unit Processes. *AICE Symp. Ser., 70*(136):367-377, 1974.
4. Unpublished data, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio.

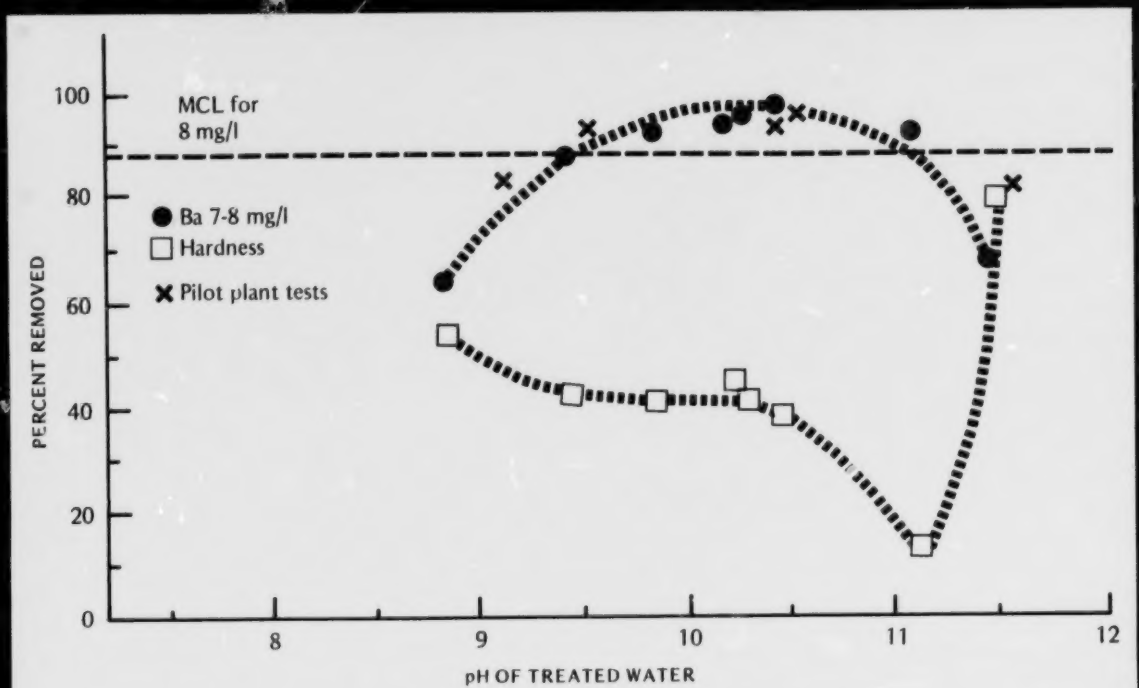


FIGURE 8 BARIUM REMOVAL BY LIME SOFTENING (1)

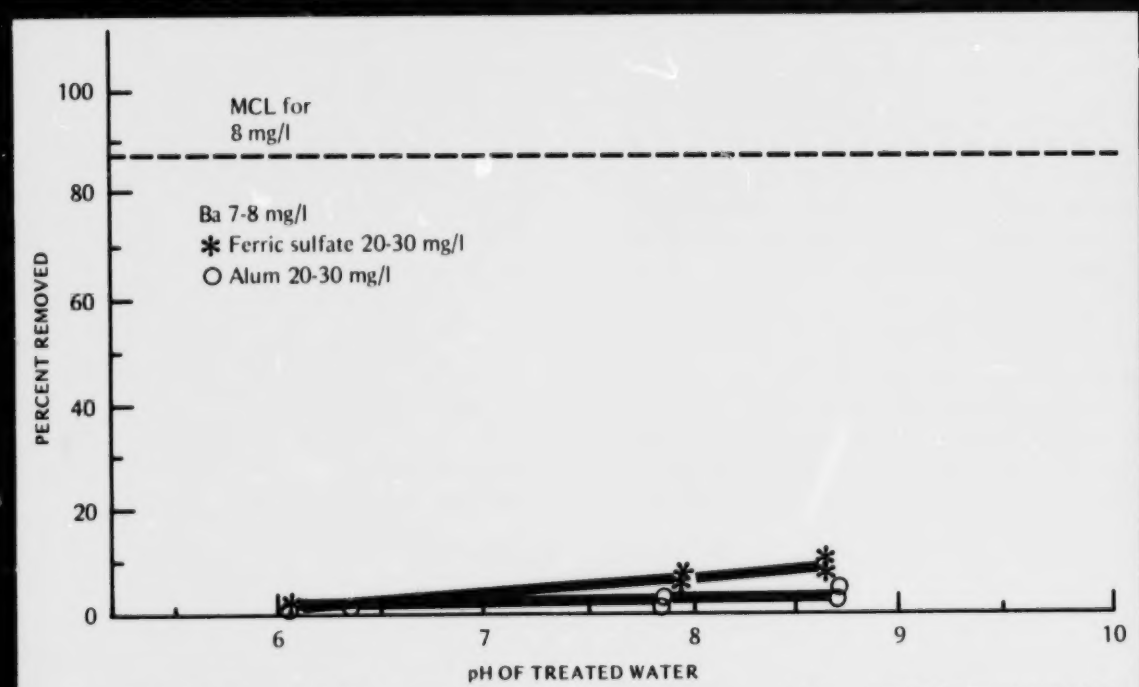


FIGURE 9 BARIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION (1)

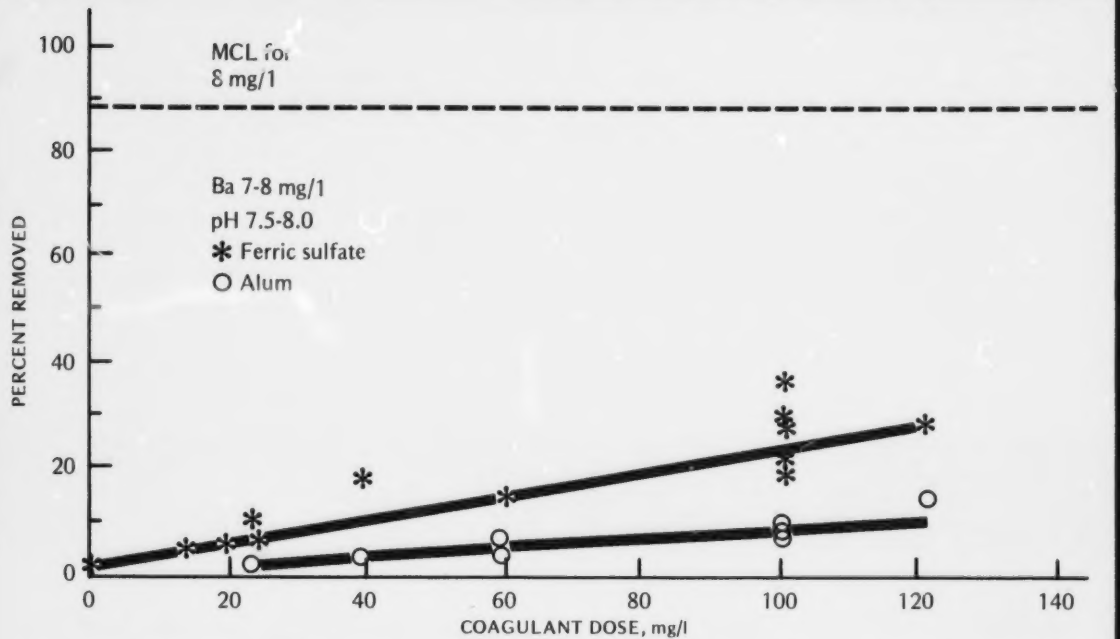


FIGURE 10 BARIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION (1)

Cadmium (Cd)

MCL: 0.010 mg/l
Common Valence Form: +2
Most Likely Occurrence and Source of Contaminant: Surface water—industrial pollutant

REMOVAL

Laboratory experiments and pilot plant studies on the removal of cadmium from water showed cadmium to be readily removed by lime softening, and to a lesser extent by ferric sulfate and alum coagulation treatment (1). Lime softening achieved removals of greater than 98 percent in the 8.5-11.3 pH range on well water containing 0.3 mg/l of cadmium (fig. 11). Removals equally as good were obtained at pH 11.2-11.3 when the initial cadmium concentration was increased up to 10 mg/l.

Cadmium removals by ferric sulfate and alum coagulation were lower than those of lime softening and were shown to depend on pH (fig. 12). Cadmium hydroxide and carbonate are reported to be extremely soluble below pH 7, and the coagulation studies confirmed the reports. Cadmium removals increased with increasing pH. Ferric sulfate coagulation studies on river water containing 0.3 mg/l of cadmium showed removals to increase from 20 percent at pH 7.2 to above 90 percent at pH 8 and above. Alum coagulation results on river water also increased with pH, but the results were not reproducible above pH 8. The data indicate that above pH 8, removals may depend on the turbidity of the raw water. In some tests with low turbidity water (1-10 Jtu), removals decreased as the pH increased. Poor formation of alum floc above pH 8 is probably another reason for the lower removal results (1).

The pH effect was also observed with ferric sulfate and alum coagulation when the low turbidity well water was used as the test water. In these laboratory studies, ferric sulfate achieved higher removals than alum, and removals increased as the pH increased above pH 7.

Studies on the effect of varying the initial cadmium concentration showed that removals decreased only slightly as the concentration increased when all other conditions remained constant. Laboratory studies also showed that cadmium removals by ferric sulfate and alum coagulation can be increased by increasing the amount of coagulant (fig. 13).

REFERENCE

1. Unpublished data, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio.

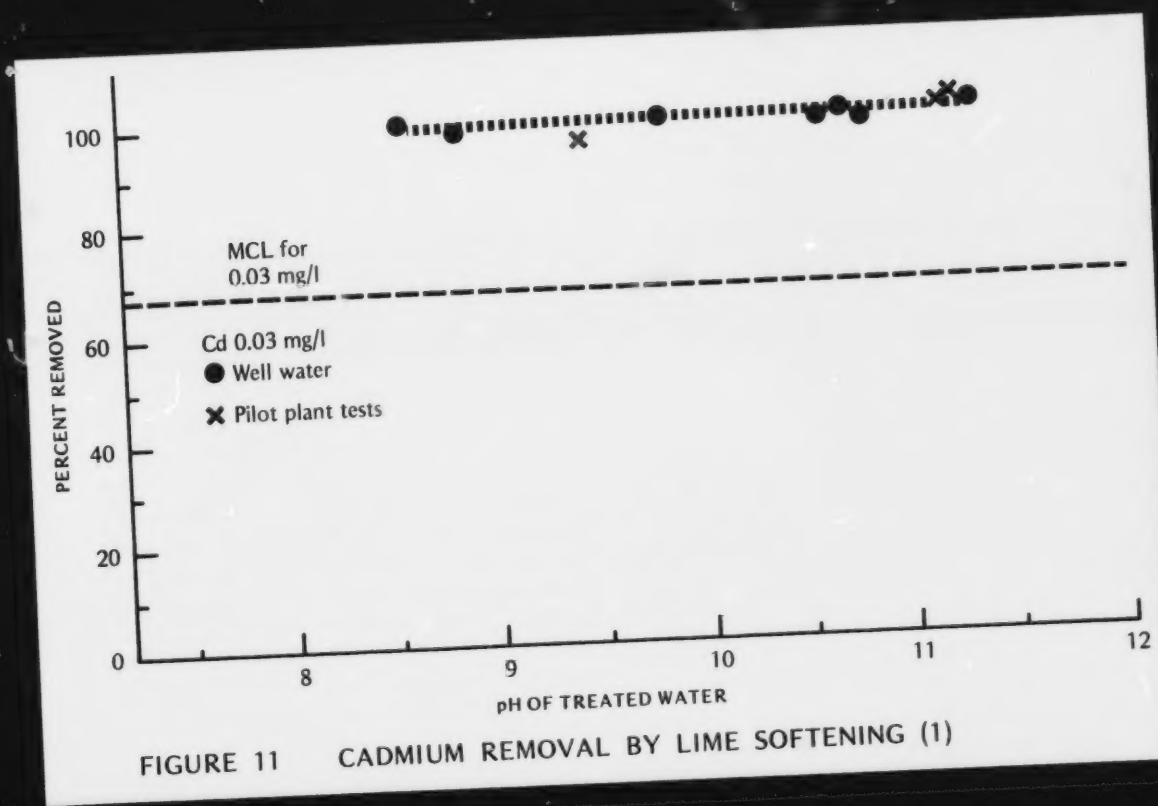


FIGURE 11 CADMIUM REMOVAL BY LIME SOFTENING (1)

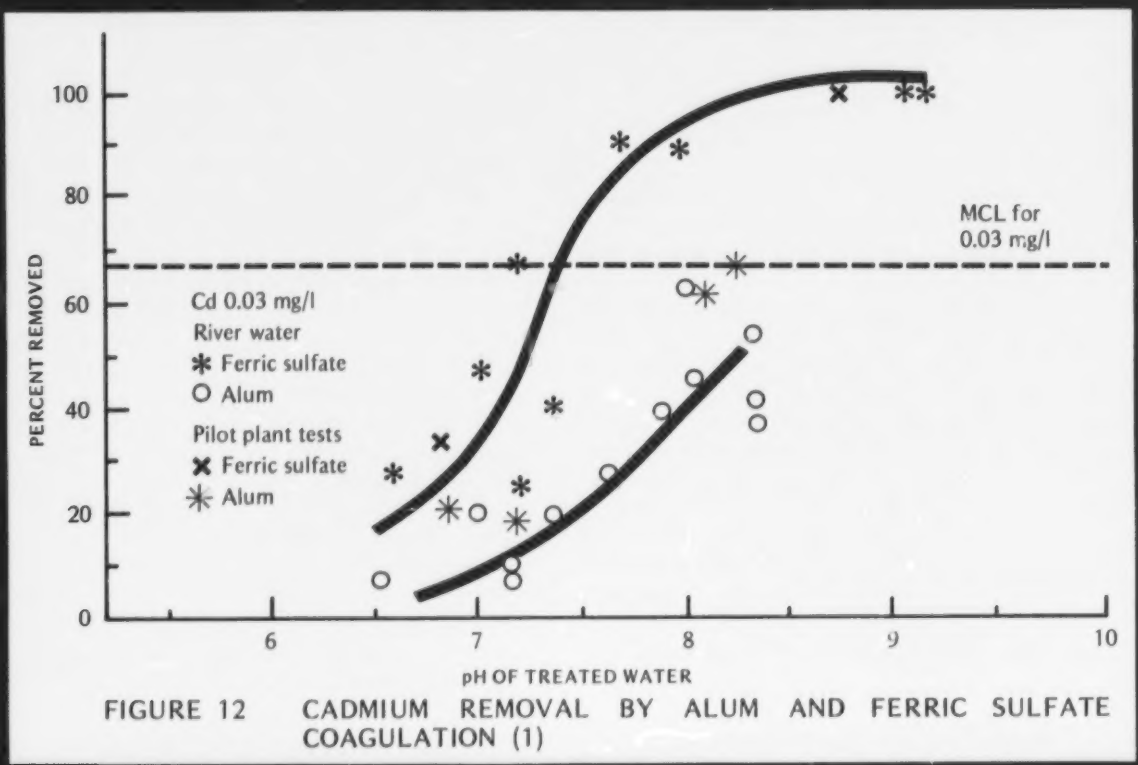


FIGURE 12 CADMIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION (1)

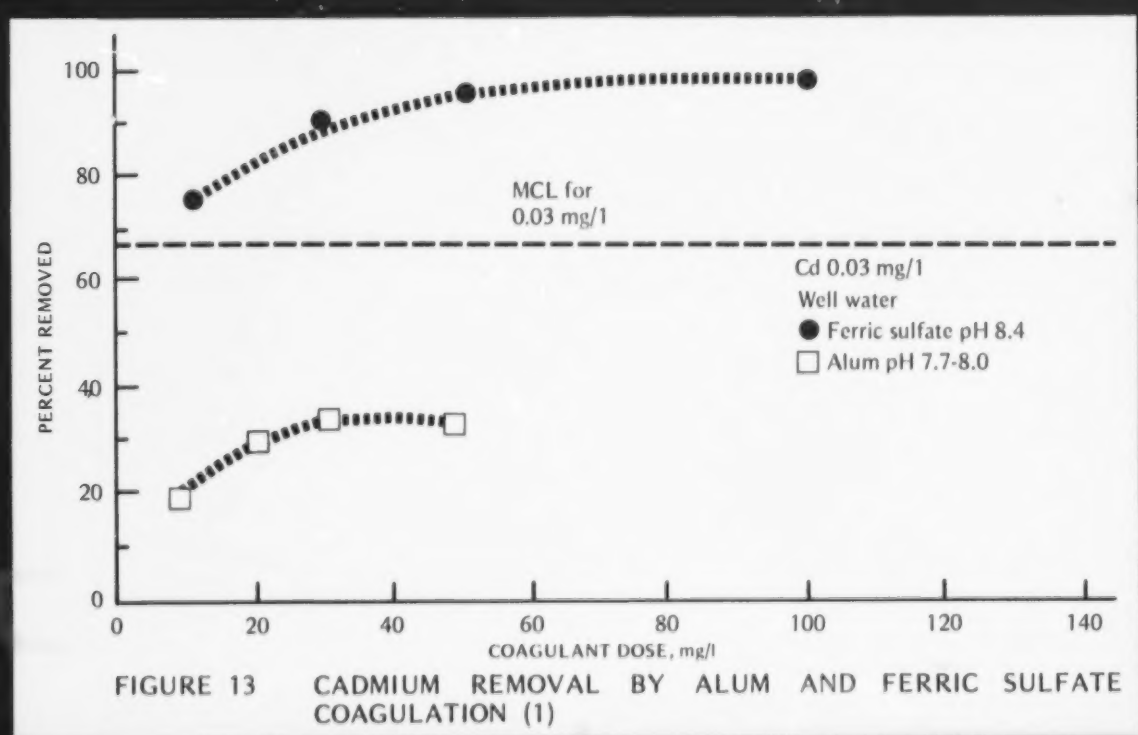


FIGURE 13 CADMIUM REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION (1)

Chromium (Cr)

MCL: 0.05 mg/l
Common Valence Forms: +3
+6

Most Likely Occurrence and Source of Contaminant:
+3 Ground water—natural occurrence
+6 Surface water—industrial pollutant

There are two common valence forms of chromium, Cr^{+3} and Cr^{+6}. In aqueous solutions, Cr^{+3} will exist as a cation and Cr^{+6} in an anion form as either chromate (CrO_4^{-2}) or dichromate ($Cr_2O_7^{-4}$) (1). The standard analytical procedures used to determine the amount of chromium in water measure only total chromium and do not distinguish between the two valence forms. Although the hexavalent form of chromium is the most toxic, the MCL was established for total chromium to minimize the analytical work load and because the hexavalent form is that most likely to be found in water. From a treatment standpoint, however, the form of the contaminant is significant because the hexavalent form is more difficult to remove from water by conventional coagulation treatment than the trivalent form. If treatment is required, the form of the chromium should be identified to select the proper type of treatment system or modification.

Cr^{+3} REMOVAL

Laboratory studies have shown that alum coagulation, iron coagulation, and lime softening are all very effective methods for removing Cr^{+3} from water (2). These studies have also shown that removals by lime softening depend on pH, whereas pH has only a very slight effect on removals by alum and iron coagulation (figs. 14 and 15). For example, lime softening achieved above 98 percent removal of Cr^{+3} (0.15 mg/l) in well water in the pH range of 10.6-11.3. Below pH 10.6, removals decreased as the pH decreased, to a low of 70 percent at pH 9.21.

Ferric sulfate achieved excellent Cr^{+3} removals—greater than 98 percent throughout the 6.5-9.3 pH range. Alum coagulation was not quite so effective as

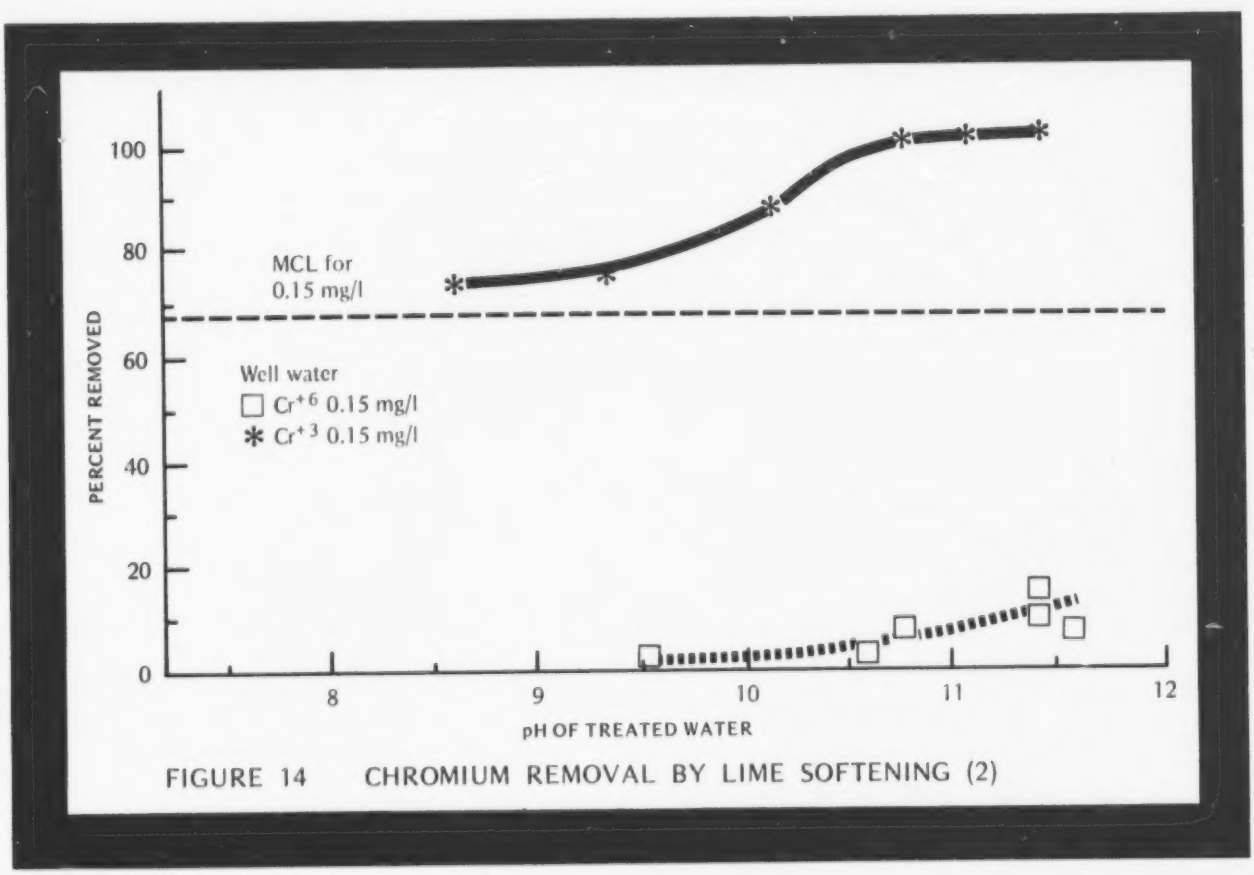


FIGURE 14 CHROMIUM REMOVAL BY LIME SOFTENING (2)

ferric sulfate, but did obtain above 90 percent removal in the 6.7-8.5 pH range. Above pH 8.5, removals began to decrease; at pH 9.2 removal dropped to 78 percent. When the Cr^{+3} concentration was increased up to 10 mg/l, ferric sulfate and alum coagulation achieved removals greater than 98 percent in the optimum pH range (fig. 16). The same excellent results were also obtained with lime softening when the Cr^{+3} concentration was increased up to 10 mg/l.

Because of the potential problem of oxidation of Cr^{+3} to Cr^{+6} by chlorination, several experiments were conducted to determine the effect of this factor. Experiments on well water containing 0.15 mg/l of Cr^{+3} showed that low chlorine doses of 2 mg/l for up to 6 hours contact time lowered Cr^{+3} removals by only about 10 percent with alum and ferric sulfate coagulation (fig. 17). When the contact time was extended to about 20 hours, however, alum removals dropped to less than 10 percent total removal. This work indicates that chlorination before treatment can oxidize Cr^{+3} to the Cr^{+6} form, which is difficult to remove, and that the extent of oxidation depends on contact time and chlorine dose. If chlorination before treatment is absolutely necessary, then ferrous sulfate is recommended as the coagulant because it has been found to be effective on Cr^{+6}.

Cr^{+6} REMOVAL

Laboratory studies on the removal of Cr^{+6} from river water showed that neither coagulation by alum or ferric sulfate nor lime softening was very effective (2). Of the three methods, ferric sulfate achieved the best results, removing 35 percent at the low pH of 5.5 on river water containing 0.15 mg/l of Cr^{+6} (fig. 18). Alum coagulation and lime softening could do no better than 10 percent removal throughout their entire pH range (figs. 14 and 18). These methods would not be recommended, therefore, unless the chromium concentration were only very slightly above the MCL.

Ferrous sulfate coagulation was studied because of its reducing characteristics as the ferrous iron oxidizes to ferric iron in the formation of the ferric hydroxide

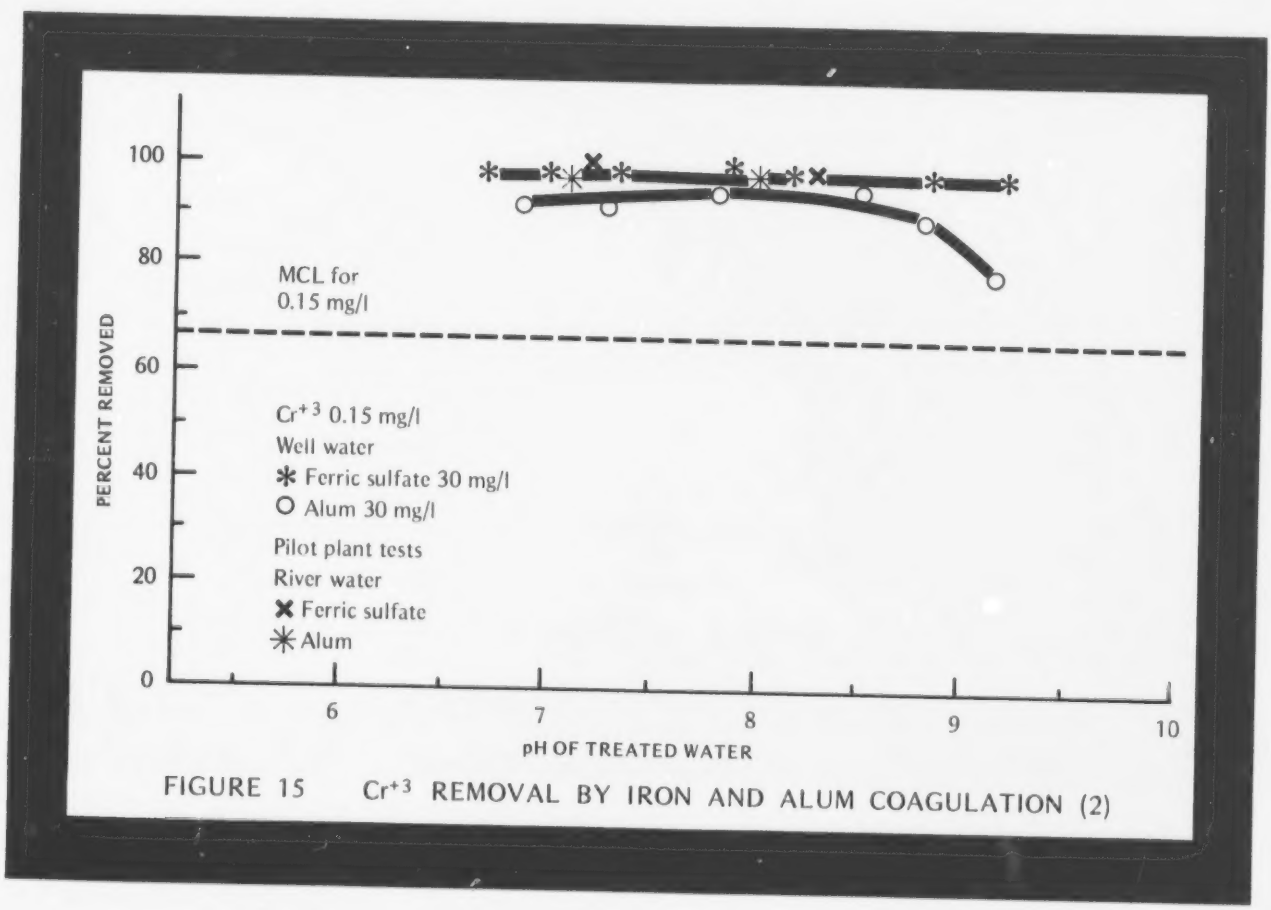


FIGURE 15 Cr^{+3} REMOVAL BY IRON AND ALUM COAGULATION (2)

floc. Studies conducted on river water containing 0.15 mg/l of Cr^{+6} showed that ferrous sulfate coagulation was capable of achieving above 98 percent removals in the 6.5-9.3 pH range (fig. 18) (1). With higher Cr^{+6} concentrations, however, it was determined that removals depend on the time of pH adjustment (fig. 19). For example, when the pH was adjusted before coagulation, Cr^{+6} removals decreased with increasing concentrations of Cr^{+6} in the raw water. Further studies showed, however, that if the pH of the water is adjusted several minutes after coagulation, removals greater than 99 percent can be achieved with Cr^{+6} concentrations of 10 mg/l. This procedure of adjusting pH after coagulation is necessary to provide time to reduce Cr^{+6} to Cr^{+3} before floc formation.

REFERENCES

1. O'Connor, J. T. Removal of Trace Inorganic Constituents by Conventional Water Treatment Processes. In: *Proceedings of the 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71 (108):99-110, 1974.
2. Unpublished data, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio.

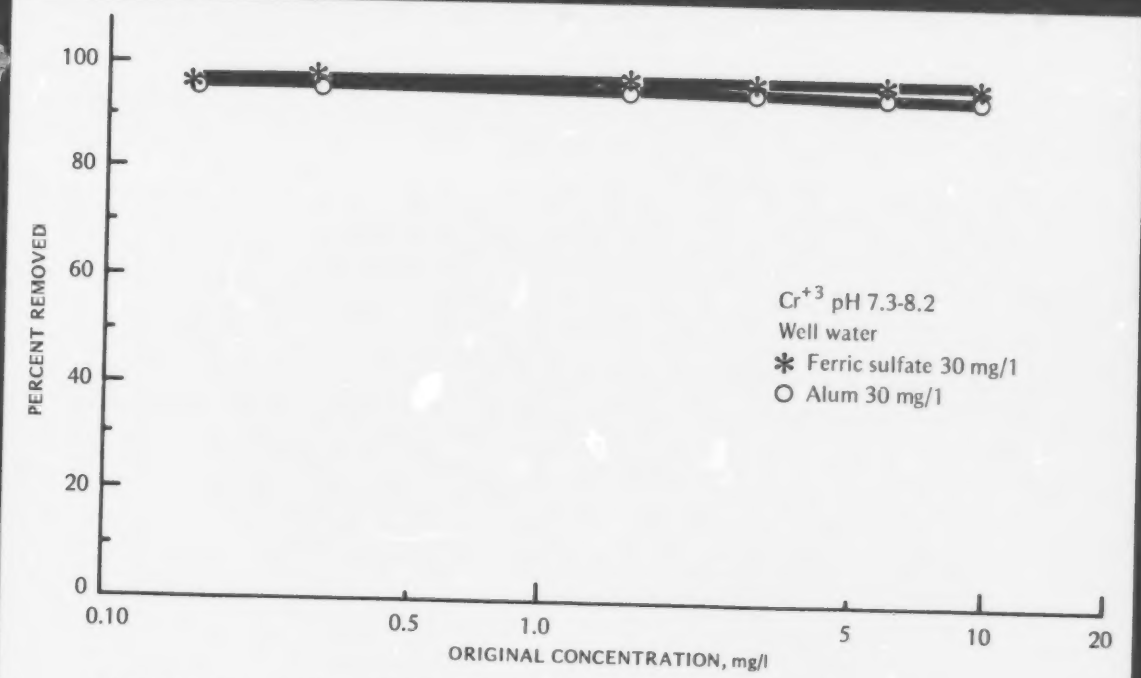


FIGURE 16 Cr^{+3} REMOVAL BY ALUM AND FERRIC SULFATE COAGULATION (2)

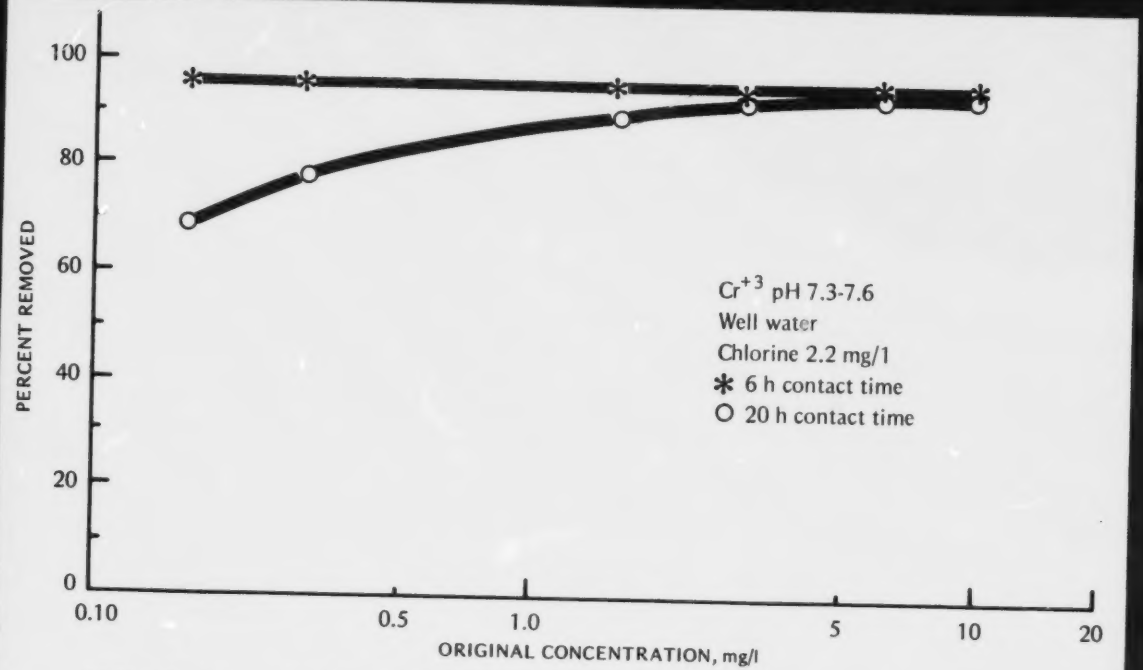


FIGURE 17 EFFECT OF PRECHLORINATION ON Cr^{+3} REMOVAL BY ALUM COAGULATION

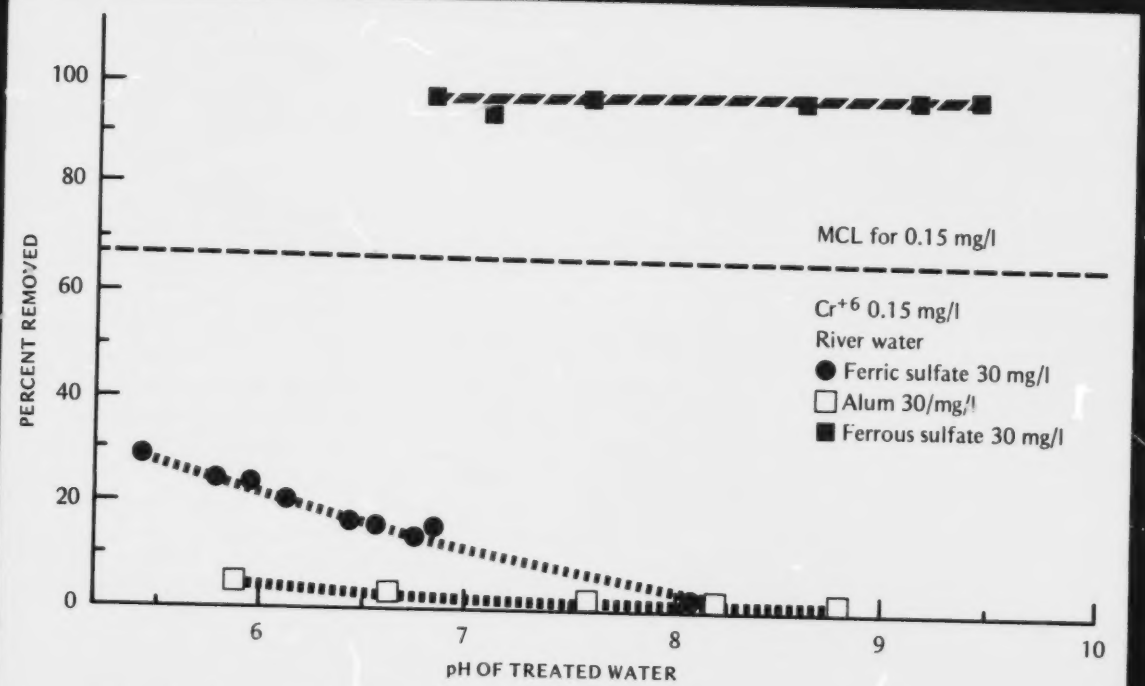


FIGURE 18 Cr^{+6} REMOVAL BY ALUM AND IRON COAGULATION (2)

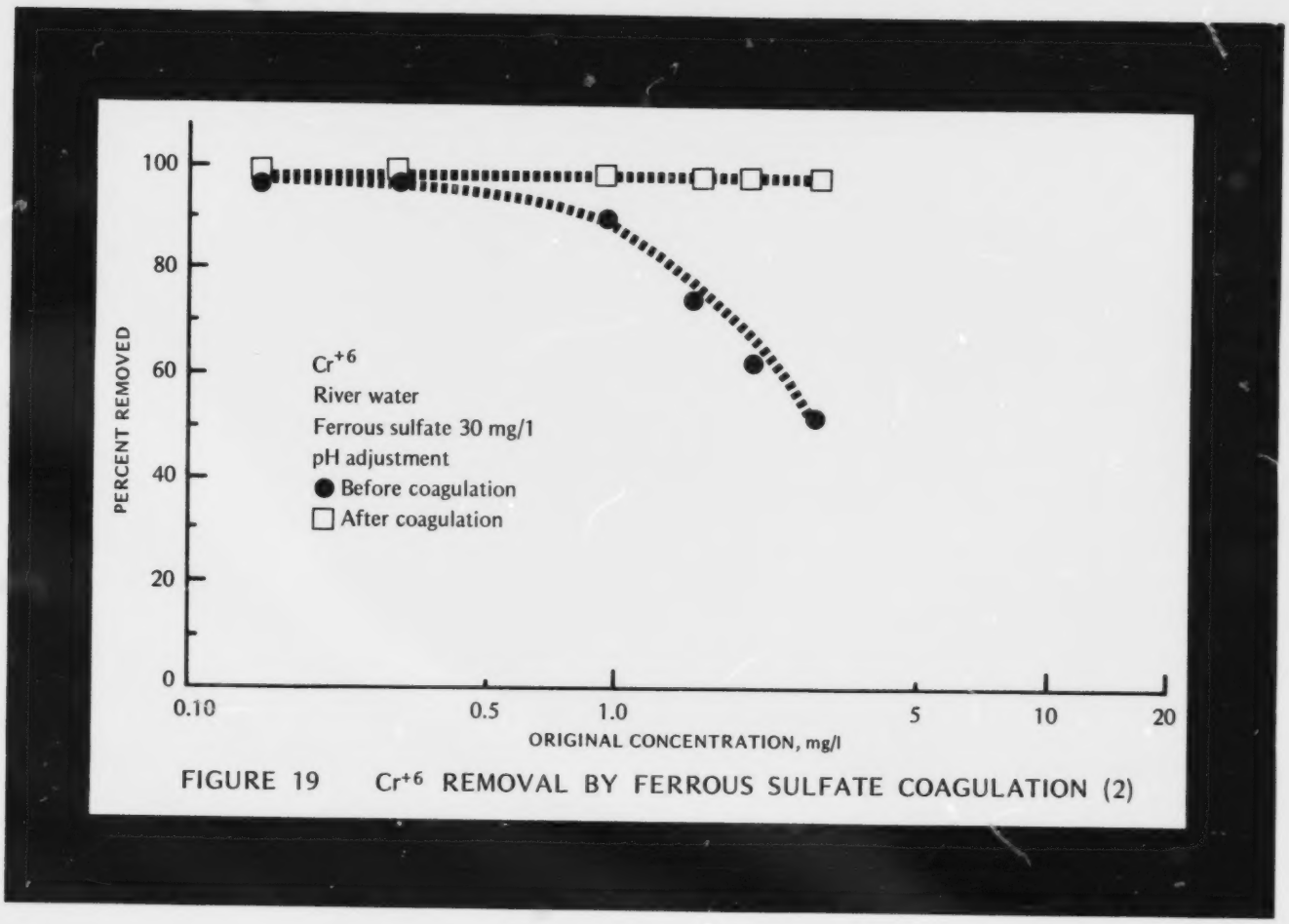


FIGURE 19 Cr^{+6} REMOVAL BY FERROUS SULFATE COAGULATION (2)

Fluoride (F)

MCL: 1.4-2.4 mg/l, depending on the annual average air temperature

Common Valence Form: -1

Most Likely Occurrence and Source of Contaminant: Ground water - natural occurrence

REMOVAL

Fluoride is added to many water supplies for the prevention of dental caries, but some communities have the problem of excessive amounts of natural fluoride in their raw water. Fluoride has been shown to be removed from water as a side reaction to excess lime softening of high magnesium water. The removal mechanism is coprecipitation with magnesium hydroxide; this process was demonstrated in Ohio in the early 1930's (1). Although excess lime softening has been shown to remove fluoride, the most common method is ion exchange (or sorption) using either bone char or activated alumina as the exchange resin. Bone char is ground animal bones charred to remove all organic matter. Activated alumina is calcined granules of hydrated alumina. Both materials are readily available.

Laboratory studies verified by actual plant practice have also shown that efficiency of removal of fluoride with bone char and activated alumina is pH dependent. The lower the pH, the more effective the

removal of fluoride. Because both materials are somewhat soluble in acid, however, and for reasons of distribution and consumption, a pH slightly above 7 is recommended. The capacities for fluoride removal for both materials are somewhat similar, and both are amenable to regeneration procedures. The media should be selected based on laboratory tests on the water to be treated to determine which material is most effective.

Both activated alumina and bone char have been used in full-scale treatment plants to remove fluoride from water. The first activated alumina plant was constructed in 1952 in Barlett, Texas (2,3). This plant was designed to lower the fluoride concentration from about 8 mg/l to less than 1 mg/l. The plant is still operating and contains much of the original activated alumina media. The operating cost is around 10 cents per 1,000 gallons of treated water. The literature also indicates that there are several other successful full-scale treatment plants using bone char and activated alumina in California (4).

Recent laboratory studies have found that arsenic can interfere with fluoride removal with bone char (5). Arsenic has been shown to be removed readily from water by both bone char and activated alumina. The investigations showed that arsenic sorption on bone char results in an irreversible change in the structure of the char and ultimately renders it useless for fluoride removal. On the other hand, activated alumina is readily regenerated when both fluoride and arsenic are removed. If, therefore, the raw water contains arsenic as well as fluoride, activated alumina would be the recommended media to use for fluoride removal. Bone char could be selected, but it would have to be thrown away when no longer effective for fluoride removal.

REFERENCES

1. Scott, R. D., A. E. Kimberley, H. L. Van Horn, F. F. Ey, and F. W. Waring, Jr. Fluorides in Ohio Water Supplies. *J. Am. Water Works Assoc.*, *29*(9):9-25, 1937.
2. Maier, F. J. Defluoridation of Municipal Water Supplies. *J. Am. Water Works Assoc.*, *45*(8): 879-888, 1953.
3. Maier, F. J. Partial Defluoridation of Water. *Public Works, 91*:90-92, 1960.
4. Harmon, J. A., and S. B. Balichman. Defluoridation of Drinking Water in Southern California. *J. Am. Water Works Assoc., 57*(2):245-254, 1965.
5. Bellack, E. Arsenic Removal from Potable Water. *J. Am. Water Works Assoc., 63*(7):454-458, 1971.

Lead (Pb)

MCL: 0.05 mg/l
Common Valence Form: +2
Most Likely Occurrence and Source of Contaminant: Surface water—industrial pollutant

REMOVAL

Literature on the solubility of lead indicates that the carbonate and hydroxide forms are very insoluble, and, therefore, lead should be removed easily from water by conventional treatment methods (1). Laboratory studies on the removal of lead by conventional treatment confirmed this finding (2,3). Ferric sulfate and alum coagulation achieved greater than 97 percent removals on river water containing 0.15 mg/l of lead in the pH range of 6-10 (figs. 20 and 21). Experiments on well water under similar test conditions showed ferric sulfate to achieve the same high removals, greater than 97 percent, while alum obtained slightly lower removals, 80-90 percent. When the lead concentration was increased up to 10 mg/l, ferric sulfate continued to achieve excellent removals of greater than 95 percent, whereas alum achieved only about 80 percent (fig. 22).

Lime softening was also studied. Experiments on well water with 0.15 mg/l of lead showed that this treatment method could achieve greater than 98 percent removals in the 8.5-11.3 pH range (fig. 23).

Because of the low solubility of the hydroxide and carbonate of lead and the ease of removal by conventional treatment, several experiments were conducted on lead removal by settling alone without a coagulant. These tests showed lead removals of 85-90 percent by 1 hour of settling of river water having a turbidity in the range of 9-40 Jtu (3). The results indicate that surface waters should normally contain very low amounts of lead because of the natural settling process of streams and impoundments.

REFERENCES

1. Hem, J. D., and W. H. Durum. Solubility and Occurrence of Lead in Surface Water. *J. Am. Water Works Assoc., 65*(8):562-568, 1973.
2. Naylor, L. M., and R. R. Dague. Simulation of Lead Removal by Chemical Treatment. *J. Am. Water Works Assoc., 67*(10):560-565, 1975.
3. Unpublished data, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio.

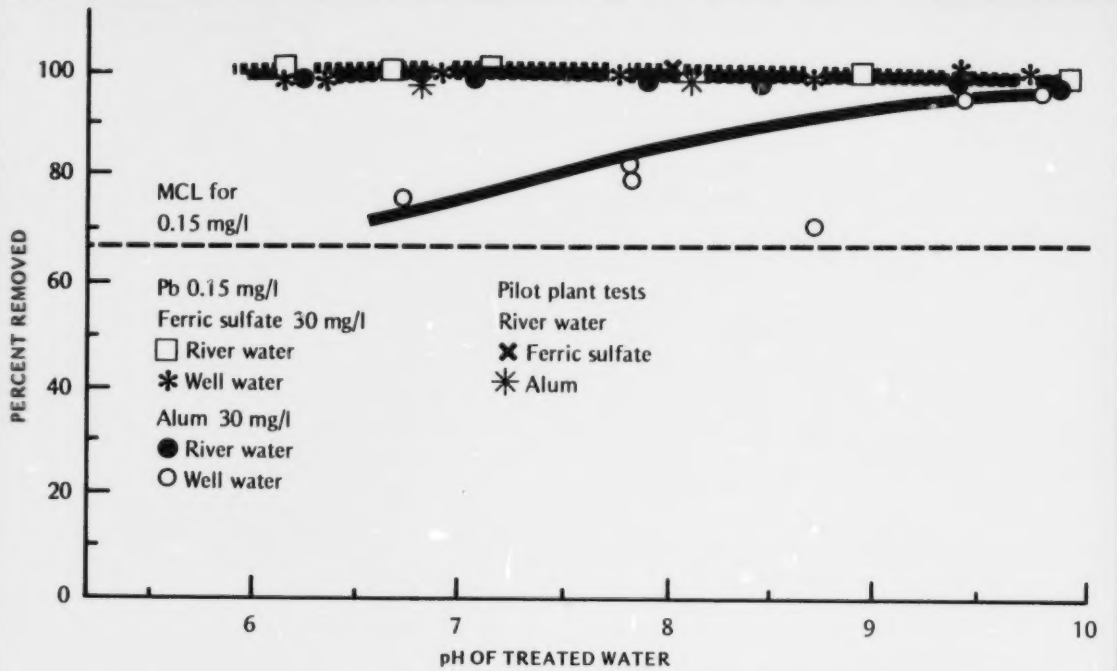


FIGURE 20 LEAD REMOVAL BY ALUM AND IRON COAGULATION (3)

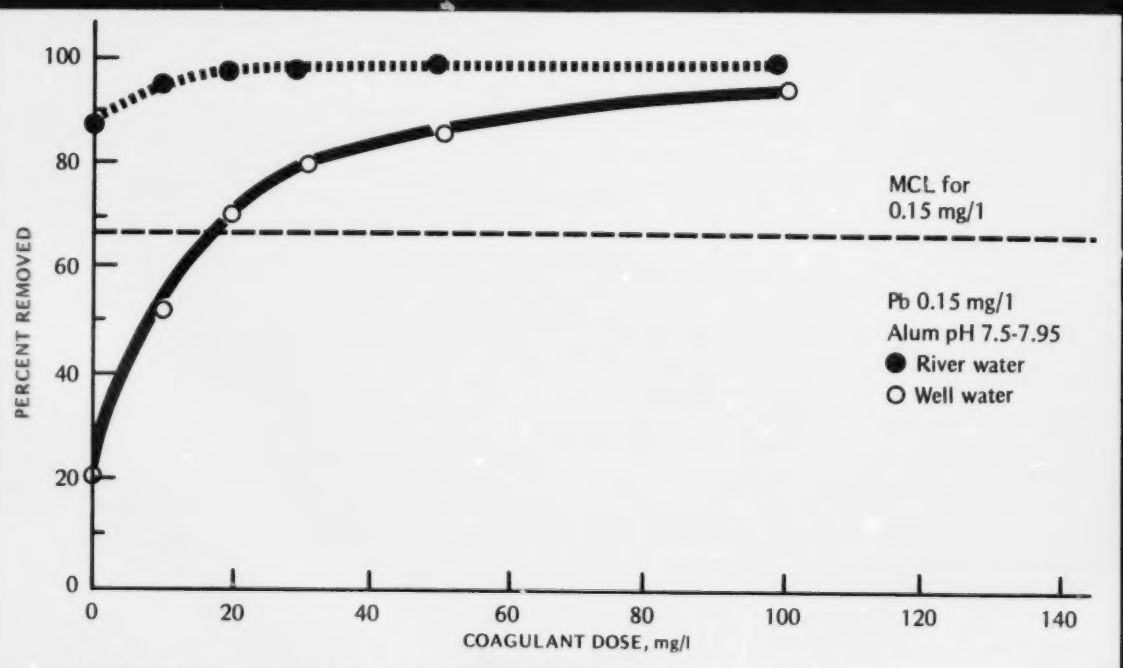


FIGURE 21 LEAD REMOVAL BY ALUM COAGULATION (3)

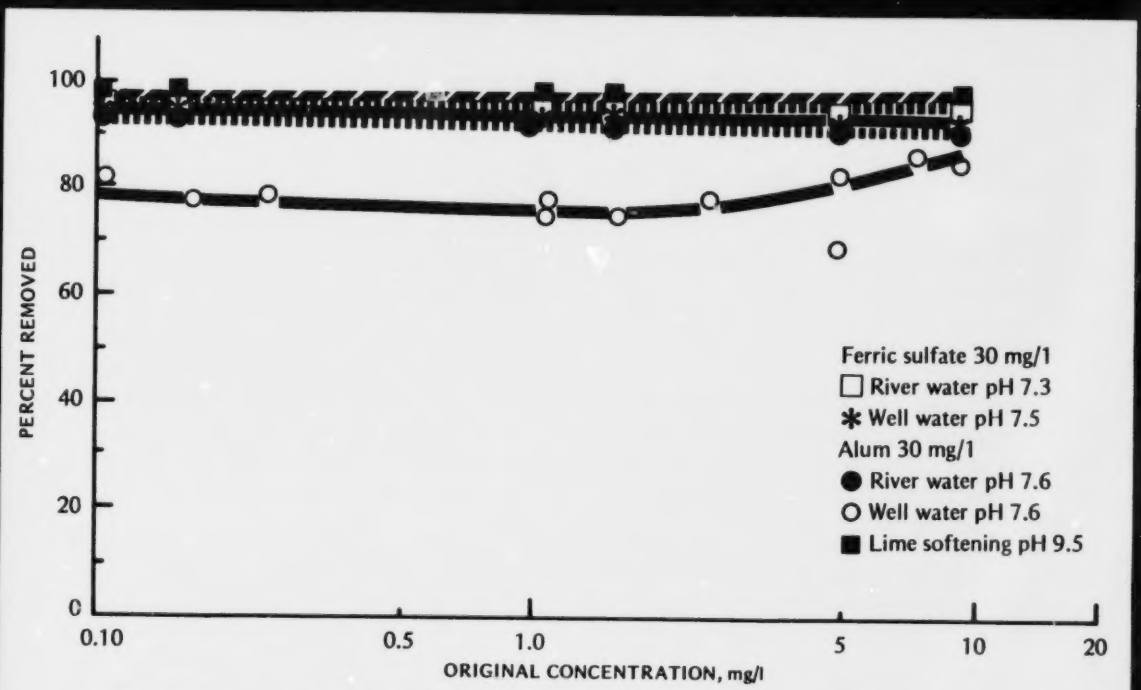


FIGURE 22 LEAD REMOVAL BY COAGULATION AND LIME SOFTENING (3)

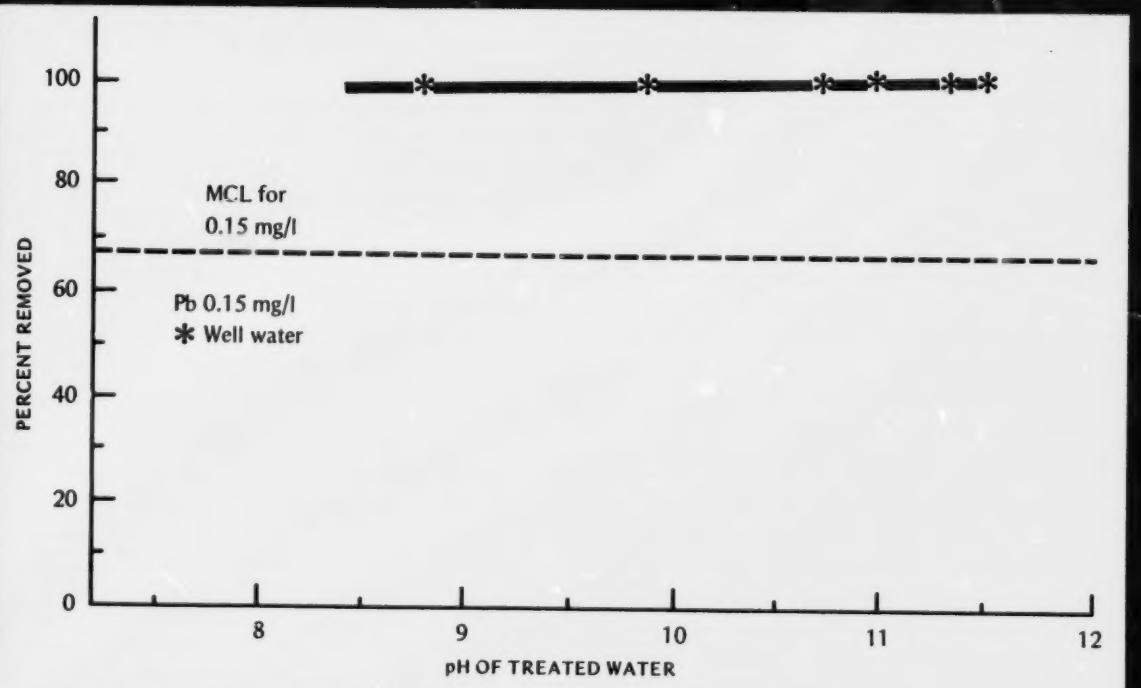


FIGURE 23 LEAD REMOVAL BY LIME SOFTENING (3)

Mercury (Hg)

MCL: 0.002 mg/l

Common Valence Forms: +2 mercury may be found in the organic or inorganic form

Most Likely Occurrence and Source of Contaminant: Surface water—industrial pollutant

Mercury may occur in either the inorganic form or organic form. The organic form is the most important because it is the more toxic of the two and is the basis for establishing the limit in drinking water. Furthermore, organic mercury is the form most likely to be found in water, and the more difficult form to remove by conventional treatment. Consequently, the form of the mercury contaminant should be determined to select the proper treatment method.

INORGANIC MERCURY REMOVAL

Laboratory experiments and pilot plant studies on the removal of mercury from drinking water have been conducted by several investigators (1,2). These studies showed inorganic mercury removals to depend on pH of the treated water and turbidity. They also showed that removals had little dependence on the mercury concentration in the 0.003-0.116-mg/l range (2). The best pH range reported for alum and iron coagulation was 7-8 (1). Ferric sulfate coagulation, 17.8 mg/l, achieved 66 percent removal at pH 7 and 97 percent removal at pH 8 on water containing 0.05 mg/l of inorganic mercury. Alum coagulation was shown to be much less effective; 47 percent of the mercury was removed at pH 7 and 38 percent at pH 8.

Turbidity of the raw river water was shown to be important only with alum coagulation. With 20-30 mg/l of alum, mercury removals increased from about 10 percent on 2-Jtu water to 60 percent on 100-Jtu water (fig. 24). Similar studies with ferric sulfate showed turbidity to be less important, with removals ranging from 30 to 60 percent (fig. 25).

Lime softening was moderately effective for inorganic mercury removal and was pH dependent (2). Removals increased as the pH increased from 8.5 to 11. In the 10.7-11.4-pH range, removals were 60-80 percent, whereas only about 30 percent removal was achieved at pH 9.4 (fig. 26).

Powdered and granular activated carbon were studied for inorganic mercury removal (2). Powdered activated carbon was shown to increase removals above those obtained with coagulation alone (fig. 27). Much higher doses would be required to produce significant increases, however, than those normally used for taste and odor control. Granular activated carbon was found to be fairly effective, although removals depend on contact time and amount of water treated. Removals of 80 percent of 20-29 μg/l of mercury were achieved with 3.5 minutes' contact time for up to 15,000 bed volumes of treatment (fig. 28).

Several preliminary ion exchange experiments have been carried out for inorganic mercury removal (2). These studies showed that as much as 98 percent of inorganic mercury added to distilled water could be removed by cation and anion exchange resins operated in series. Although these experiments were very preliminary, the results indicated that ion exchange should be an effective method for inorganic mercury removal.

ORGANIC MERCURY REMOVAL

Laboratory experiments and pilot plant studies have shown organic mercury to be more difficult to remove from drinking water by conventional treatment methods than inorganic mercury (1,2). Alum and iron coagulation achieved lower organic mercury removals than inorganic mercury under the same initial test conditions. Studies on the effect of turbidity on removal showed alum coagulation removals to increase from 0 to about 40 percent when the turbidity increased from 2 Jtu to 100 Jtu (fig. 24). Removals with ferric sulfate coagulation were almost identical to the alum coagulation results. Lime softening was studied and found ineffective for organic mercury removal; less than 5 percent was removed in the pH range of 9.3-11.3 (fig. 25).

Preliminary studies were also carried out on ion exchange for organic mercury removal (2). Results of these studies were similar to those on inorganic mercury, with above 98 percent removals achieved by passing distilled water containing organic mercury through cation and anion exchange resins. These results also indicate that ion exchange should be effective for organic mercury removal.

Powdered and granular activated carbon were investigated for organic mercury removal and both were found to be effective (2). Studies showed that about 1 mg/l of powdered activated carbon is needed to remove each 0.1 µg/l of mercury from water to reach a residual level of 2 µg/l. Studies on the use of granular activated carbon showed that removals depend on contact time and the amount of water treated similar to the finding for inorganic mercury. Mercury removals of 80 percent or above were achieved for 25,000 bed volumes of water with 3.5 minutes contact time on water containing 20-29 µg/l of organic mercury (fig. 29).

REFERENCES

1. Eberson, G., and J. T. O'Connor. The Removal of Mercury from Water by Conventional Water Treatment Processes. Presented at 92nd Annual Conference, American Water Works Association, Chicago, Ill., June 1972.
2. Logsdon, G. S., and J. M. Symons. Mercury Removal by Conventional Water Treatment Techniques. *J. Am. Water Works Assoc.*, 65(8):554-562, 1973.

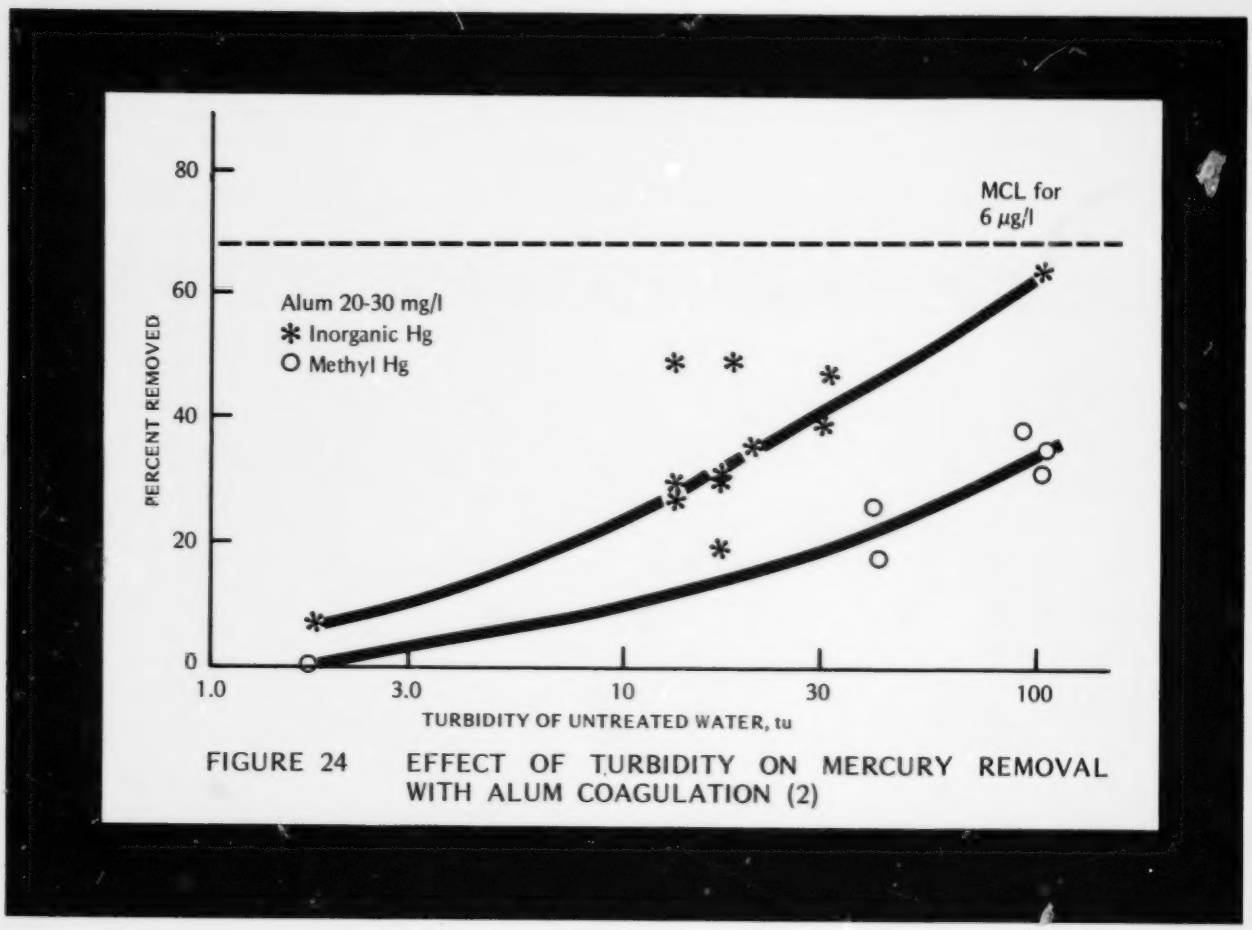


FIGURE 24 EFFECT OF TURBIDITY ON MERCURY REMOVAL WITH ALUM COAGULATION (2)

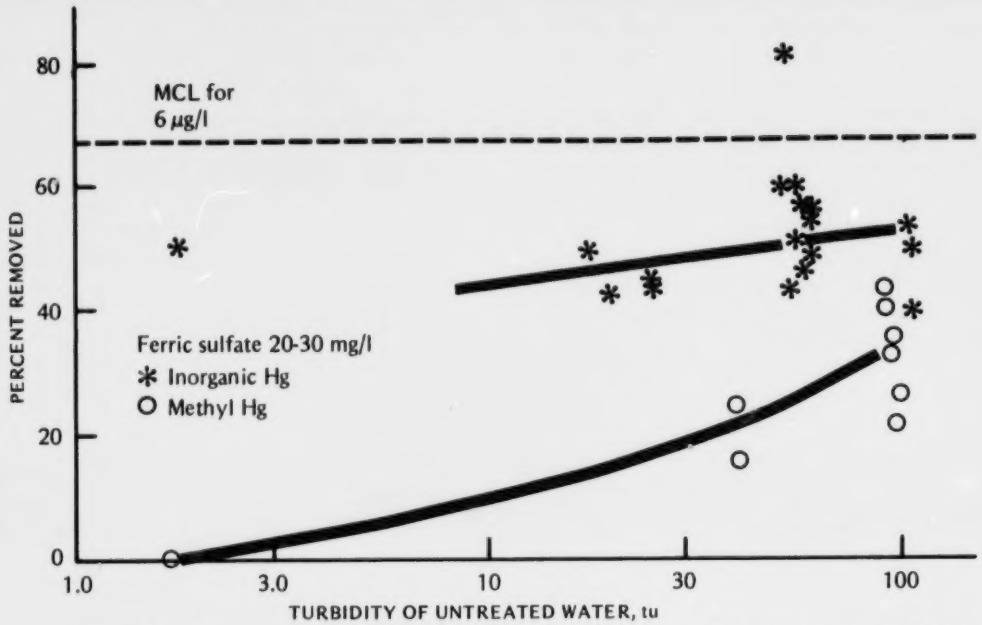


FIGURE 25 EFFECT OF TURBIDITY ON MERCURY REMOVAL WITH IRON COAGULATION (2)

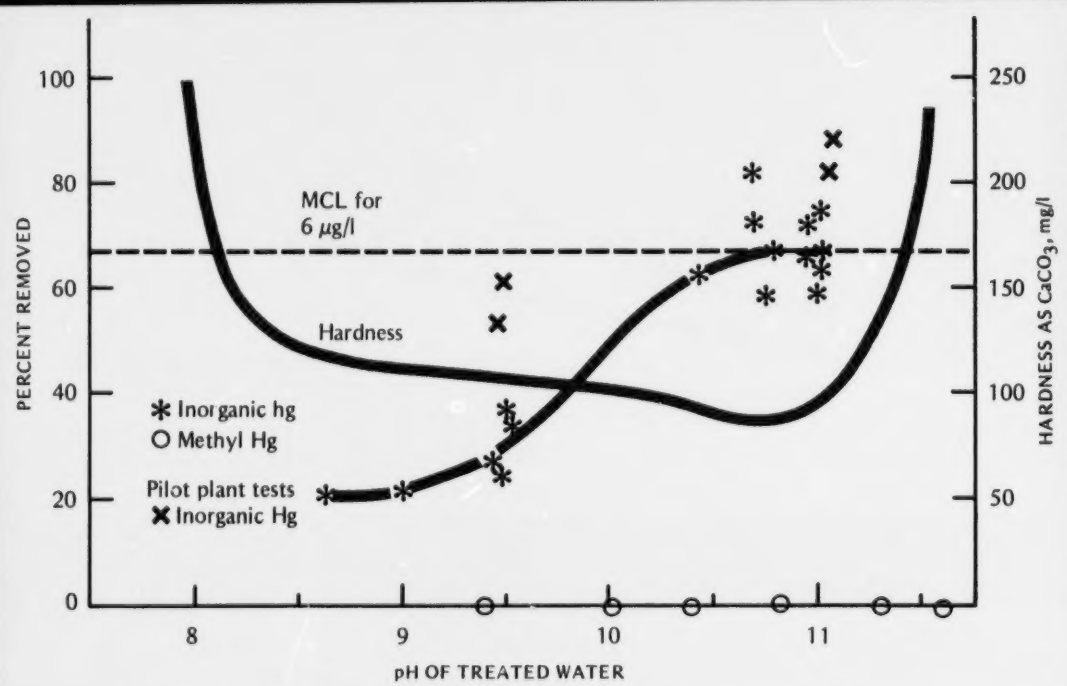


FIGURE 26 MERCURY REMOVAL BY LIME SOFTENING (2)

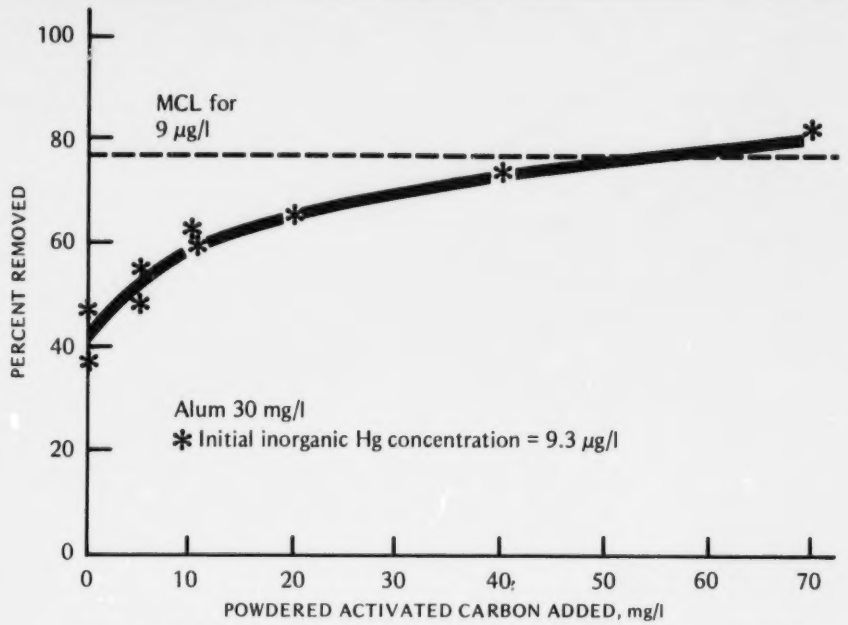


FIGURE 27 MERCURY REMOVAL BY POWDERED ACTIVATED CARBON (2)

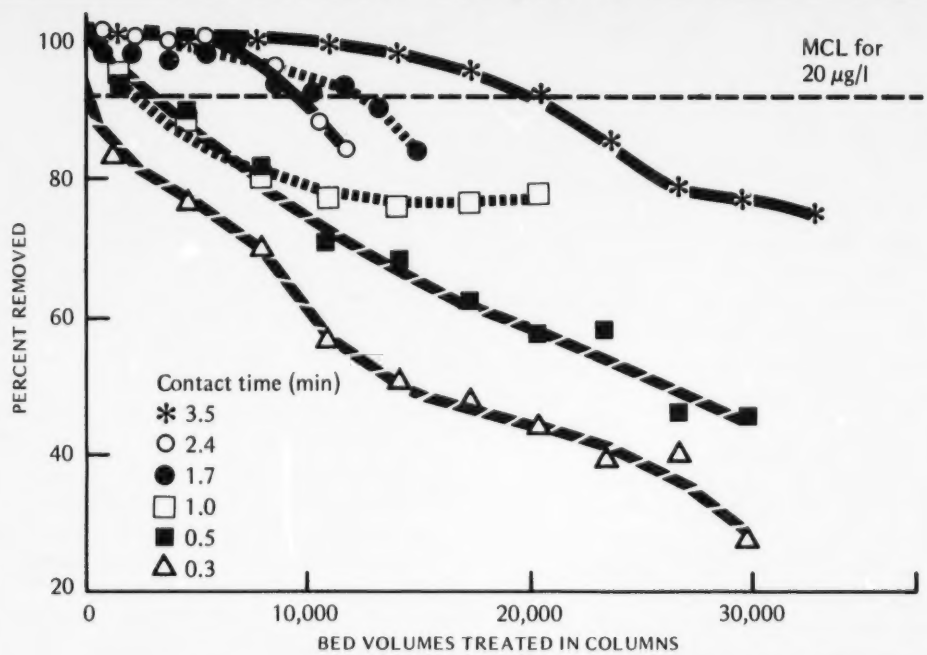


FIGURE 28 ORGANIC MERCURY REMOVAL BY GRANULAR ACTIVATED CARBON COLUMNS (2)

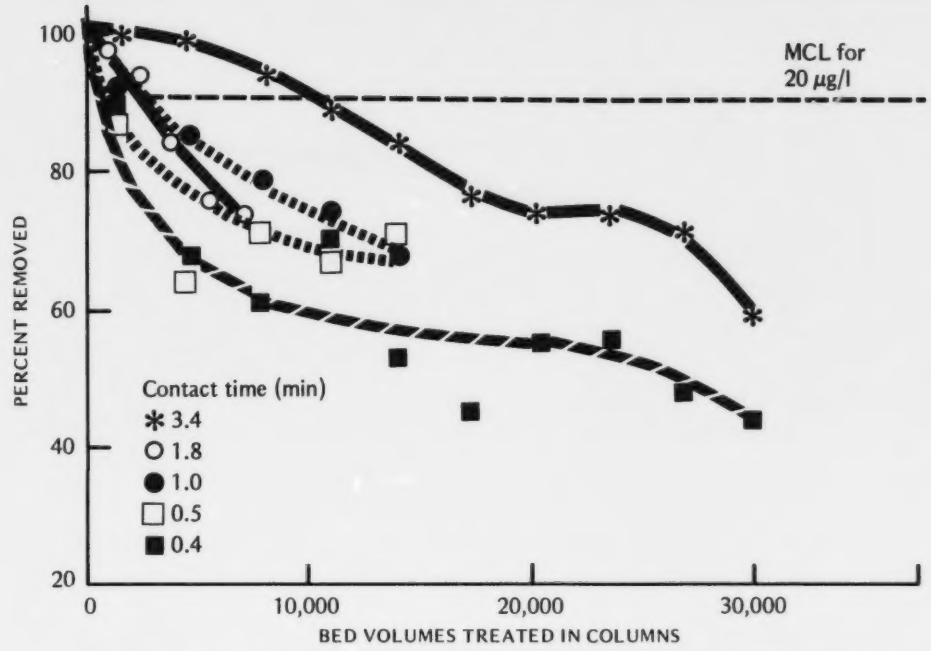


FIGURE 29 INORGANIC MERCURY REMOVAL BY GRANULAR ACTIVATED CARBON COLUMNS (2)

Nitrate (NO_3)

MCL: 45 mg/l (10 mg/l as N)
Common Valence Form: -1
Most Likely Occurrence and Source of Contaminant:
Ground water—agricultural pollutant
Surface water—agricultural pollutant

REMOVAL

Ion exchange is currently the only method in use to remove nitrate from water. Conventional coagulation and lime softening are not effective treatment methods for the removal of this contaminant.

Laboratory experiments and pilot plant studies have shown that some strong base and weak base ion exchange resins are nitrate selective and can reduce the nitrate concentration from as high as 50 mg/l (as N) to 0.5 mg/l (1-4). One full-scale ion exchange plant has been operating successfully in Long Island, New York, since 1974 (2). This plant lowers the nitrate level of 20-30 mg/l in the raw water to 0.5 mg/l. The finished water is a blend of treated and raw water, and contains about 5 mg/l of nitrate (as N). The plant was designed to treat 1,200 gal/min and incorporates a continuously regenerated ion exchange process, operated with the resin moving in a closed loop and using a strong anion exchange resin. The construction cost for the plant was $405,000 in 1974, and the estimated operating cost is 7 cents per 1,000 gallons of finished water.

Studies by EPA have shown that the nitrate selectivity of strong base resins changes with substantial changes in the ion concentrations in the water (5). Therefore, to evaluate the nitrate removal efficiency for a specific water, tests should be conducted with the actual water to be treated.

A research grant was funded by EPA to study the capability of the strong-acid/weak-base ion exchange system to remove nitrate. Preliminary results indicate

that the system will remove nitrate effectively; however, the operating cost may be about twice as much as the strong base system. The potential advantage of this system is a waste product that may have fertilizer value for agricultural uses.

REFERENCES

1. Gauntlett, R. B. Nitrate Removal from Water by Ion Exchange. *Water Treat. Exam.*, *24*(3): 172-190, 1975.
2. Gregg, J. C. Nitrate Removal at Water Treatment Plant. *Civ. Eng.*, *43*(4):45-47, 1973.
3. Holzmacher, R. G. Nitrate Removal from a Ground Water Supply. *Water Sewage Works*, *118*(7):210-213, 1971.
4. Korngold, E. Removal of Nitrates from Potable Water by Ion Exchange. *Water, Air, Soil Pollut.*, *2*:15-22, 1973.
5. Beulow, R. W., K. L. Kropp, J. Withered, and J. M. Symons. Nitrate Removal by Anion-Exchange Resins. *J. Am. Water Works Assoc.*, *67*(9):528-534, 1975.

Selenium (Se)

MCL: 0.01 mg/l
Common Valence Forms:
+4 (selenite)
+6 (selenate)
Most Likely Occurrence and Source of Contaminant:
+4 Ground water—natural occurrence
+6 Ground water—natural occurrence
Surface water—natural occurrence

The standard analytical procedures used to determine the amount of selenium in water measure only total selenium and do not distinguish between the two forms. Because of differences in removals of each form by conventional coagulation and lime softening methods, it is important that the form be determined before selecting a treatment system or modifications to an existing system. The literature indicates that the two forms are fairly stable and act independently of one another in the same solution (1). Because of this stability factor, the oxidation-reduction characteristics of the raw water should have little effect on changing the form.

The literature also indicates that selenium should be found as an anion in aqueous solutions as either SeO_3^{-2}(selenite) or SeO_4^{-2} (selenate) (2). This fact is important if ion exchange is being considered to insure that the proper ion exchange media is selected.

Se^{+4} REMOVAL

Laboratory experiments and pilot plant studies have shown that alum and ferric sulfate coagulation and lime softening are only moderately effective on the removal of Se^{+4} from water (3-6). Furthermore, these studies have shown that removals depend on pH and coagulant dose (figs. 30, 31, and 32). Ferric sulfate coagulation (30 mg/l) achieved the best results, with 85 percent removal at the low pH of 5.5 on river water containing 0.03 mg/l. Removals decreased to about 15 percent removal as the pH increased to pH 9.2. Slightly lower removals were achieved with low turbidity well water and the same pH trend of decreasing removals with increasing pH was observed.

Alum coagulation was much less effective than ferric sulfate (fig. 30). Less than 20 percent removal was achieved with 30 mg/l of alum on test waters containing 0.03 mg/l of Se^{+4} throughout the pH range. Even when the alum dose was increased to 100 mg/l at pH 6.9, only 32 percent of Se^{+4} was removed (fig. 32). Studies on the effect of the initial selenium concentration up to 10 mg/l showed that it was not a factor for removal by either coagulant.

Lime softening was also studied. Results of these tests showed that removals increased with increasing pH, but that, at best, only about 45 percent could be removed from well water containing 0.03 mg/l of Se^{+4} (fig. 31).

Very limited laboratory studies have been conducted to determine Se^{+4} removal from water by ion exchange and reverse osmosis. Both methods achieved excellent removals of greater than 97 percent on tap or distilled water containing about 0.1 mg/l of selenium (6). Although these studies were very brief and were conducted under laboratory conditions, the results indicate that both methods are capable of achieving high removals of Se^{+4}.

Se^{+6} REMOVAL

Laboratory tests and pilot plant studies have shown that alum, ferric sulfate, and ferrous sulfate coagulation and lime softening are ineffective for selenate removal from water (3-6). Studies on water containing 0.03-10 mg/l showed that none of these conventional treatment methods could achieve more than 10 percent removal. If, therefore, selenate has to be removed from water, other methods must be used.

Procedures for laboratory studies on the use of ion exchange and reverse osmosis to remove selenate from water were similar to those used for the selenite studies (6). The results of the very limited tests showed that both ion exchange and reverse osmosis could achieve greater than 97 percent removals of Se^{+6} from either tap or distilled water containing 0.1 mg/l of selenate. Although the studies were preliminary, they indicate that selenate can be removed effectively from water by these methods.

REFERENCES

1. Olson, E. E., and C. W. Jensen. The Adsorption of Selenate and Selenite Selenium by Colloidal Ferric Hydroxide. In: *Proc. S. D. Acad. Sci., 20*:115-121, 1940.
2. O'Connor, J. T. Removal of Trace Inorganic Constituents by Conventional Water Treatment Processes. In: *Proceedings of the 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71 (108):99-110, 1974.
3. Logsdon, G. S., T. J. Sorg, and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of 16th Water Quality Conference—Trace Metals in Water Supplies: Occurrence, Significance, and Control.* University of Illinois Bulletin No. 71, 1974. Pp. 111-133.
4. Logsdon, G. S., and J. M. Symons. Removal of Heavy Metals by Conventional Treatment. In: *Proceedings of a Symposium on Trace Metals in Water Removal Processes and Monitoring.* U.S. Environmental Protection Agency, New York, N.Y., 1973. Pp 225-256.
5. Logsdon, G. S., and J. M. Symons. Removal of Trace Inorganics by Drinking Water Treatment Unit Processes. *AICE Symp. Ser., 70*(136): 367-377, 1974.
6. Sorg, T. J., and G. S. Logsdon. Removal of Selenium from Water—State of the Art. Presented at 1976 Industrial Health Foundation, Inc., Symposium on Selenium-Tellurium, University of Notre Dame, Notre Dame, Ind., May 11-13, 1976.

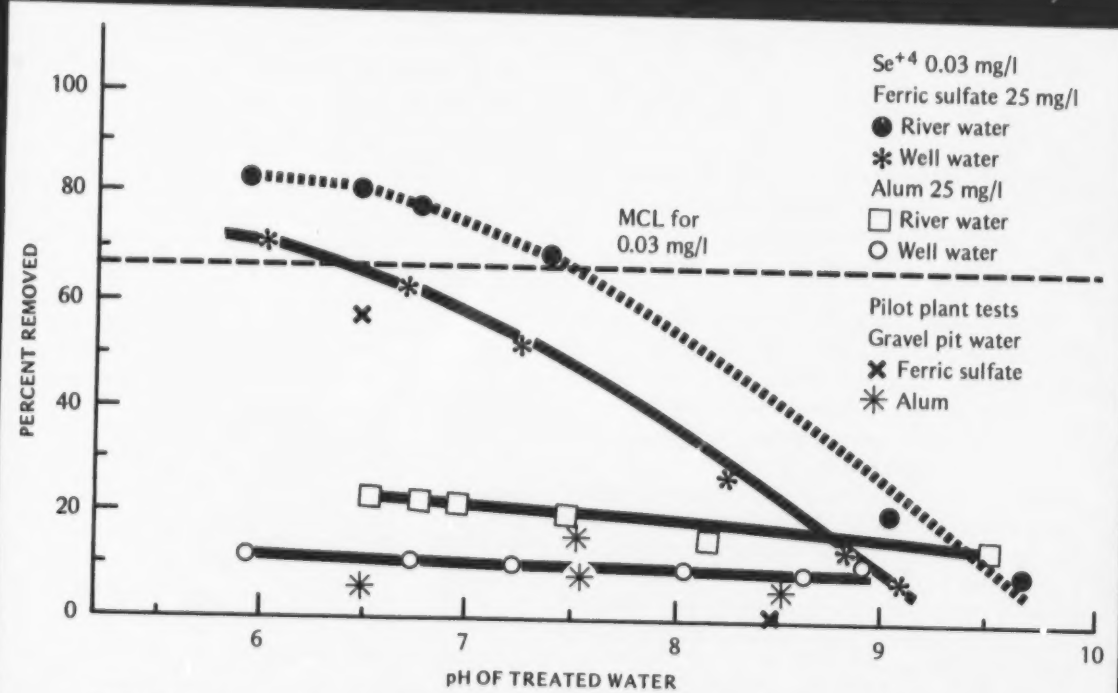


FIGURE 30 Se^{+4} REMOVAL BY ALUM AND IRON COAGULATION (6)

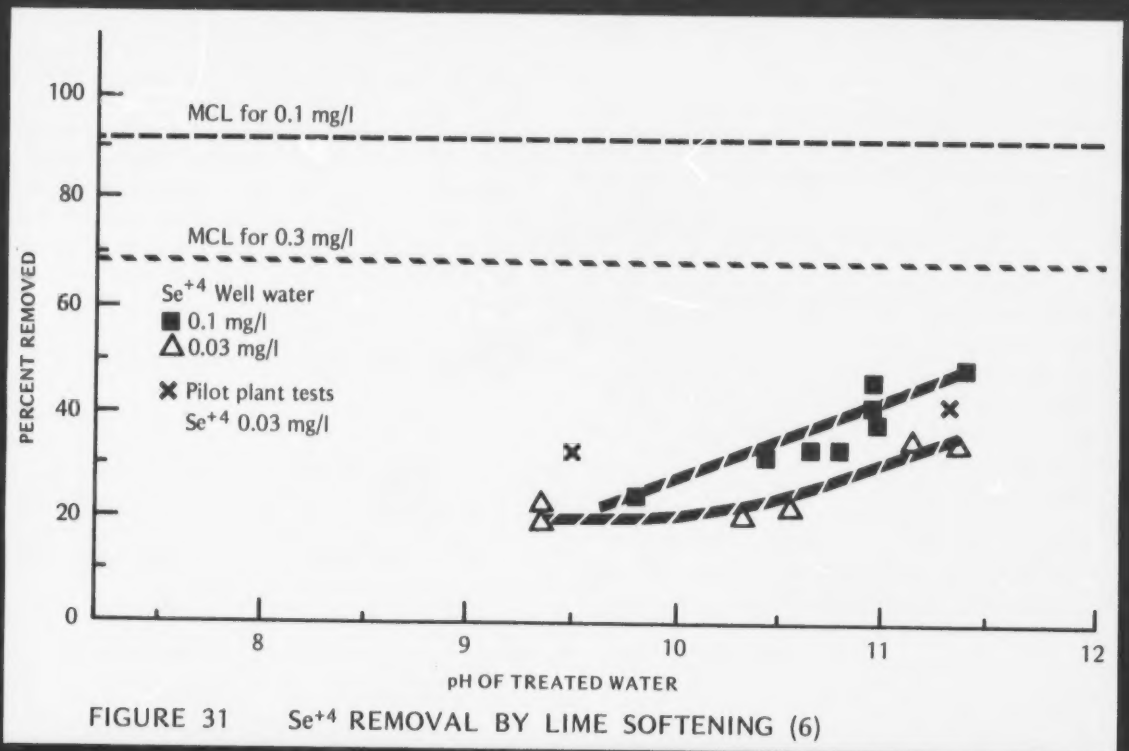


FIGURE 31 Se^{+4} REMOVAL BY LIME SOFTENING (6)

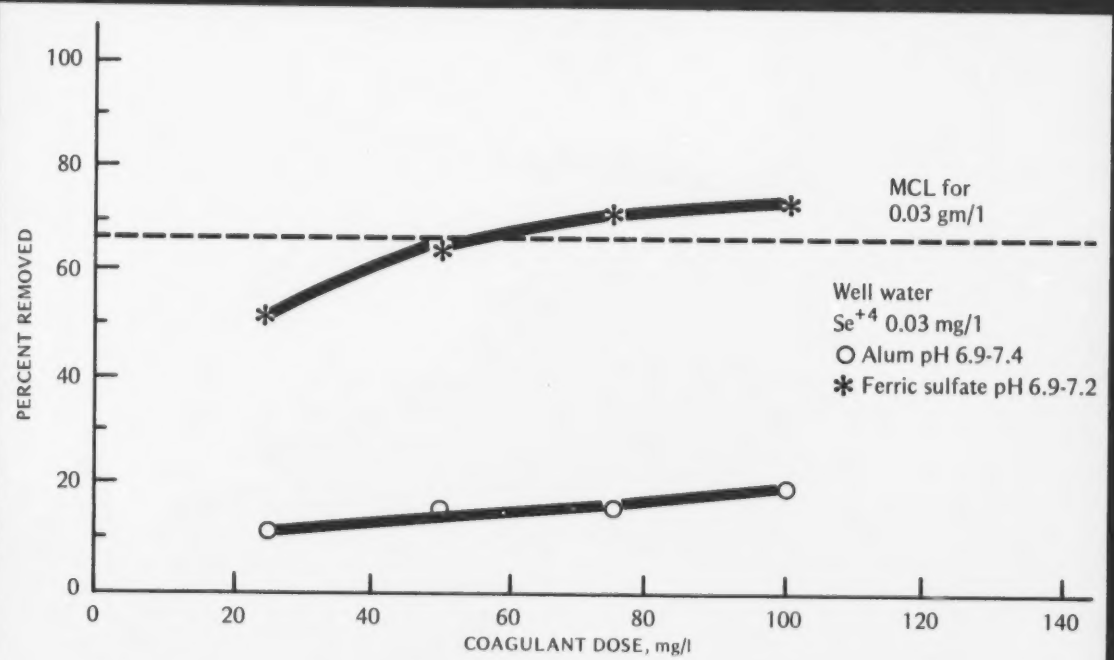


FIGURE 32 Se^{+4} REMOVAL BY ALUM AND IRON COAGULATION (6)

Silver (Ag)

MCL: 0.05 mg/l
Common Valence Form: +2
Most Likely Occurrence and Source of Contaminant:
Surface water—industrial pollutant

REMOVAL

Laboratory tests have been conducted on the removal of silver from water (1). The tests showed that silver should be easily removed from water by conventional coagulation and lime softening treatment methods. Alum and ferric sulfate coagulation achieved greater than 70 percent removal in the 6-8 pH range on river water containing 0.15 mg/l of silver (fig. 33). Above pH 8, alum removals decreased with increasing pH. This decrease is attributed to the poor alum floc formation above pH 8. Experiments with both coagulants at pH 7.9-8.0 showed removals to increase with increasing concentration from 0.15 to 10 mg/l (fig. 34).

Lime softening was also studied. Tests conducted on well water with 0.15 mg/l of silver found removals to increase with pH from about 70 percent at pH 9 to near 90 percent at pH 11.5 (fig. 35).

Because of the good removal results by chemical coagulation, the effect of settling alone without a coagulant was studied. An experiment with river water of 39-Jtu turbidity and 0.15 mg/l of silver showed that about 50 percent of the silver could be removed by settling alone. This finding indicates that silver probably should not be a serious problem in surface waters because of the natural settling process of the sediment in streams and impoundments.

REFERENCE

1. Unpublished data, U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio.

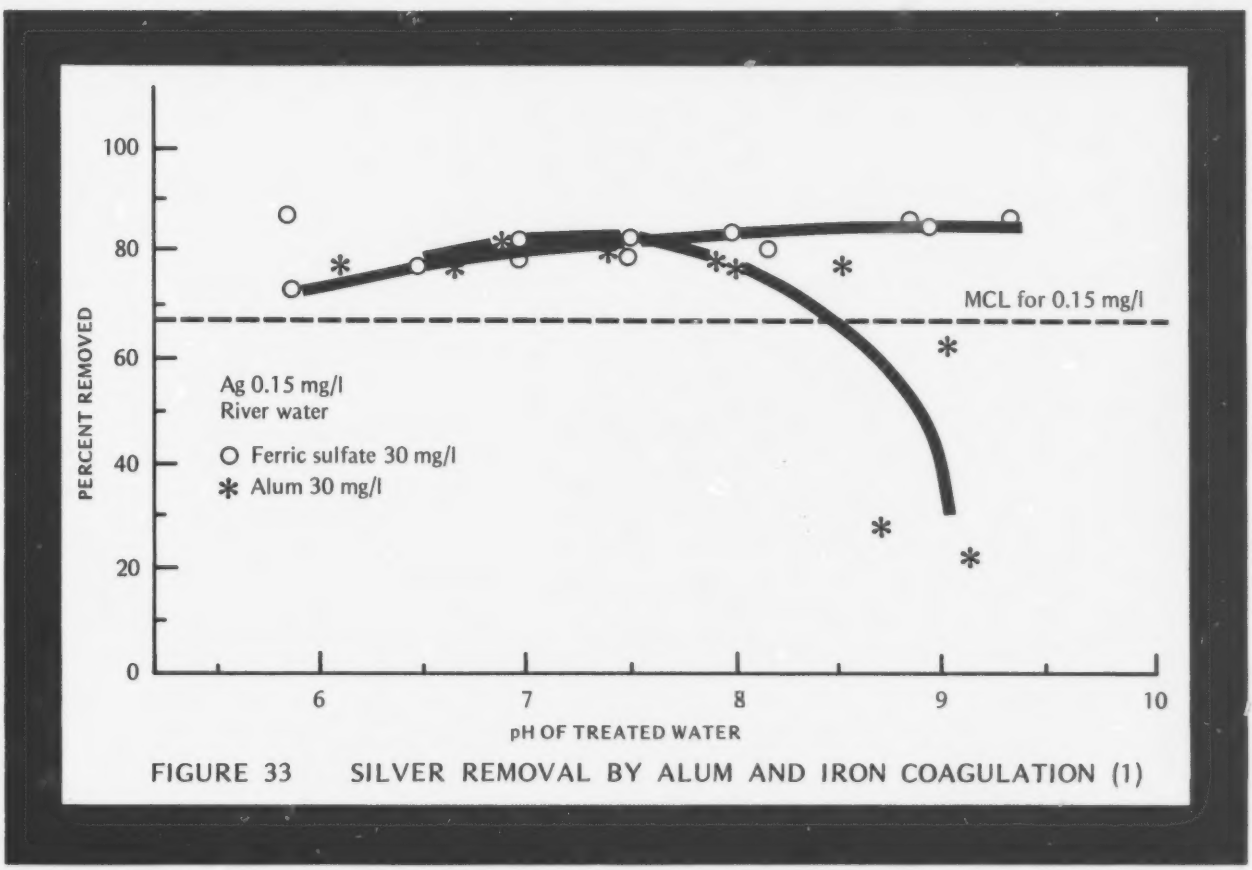


FIGURE 33 SILVER REMOVAL BY ALUM AND IRON COAGULATION (1)

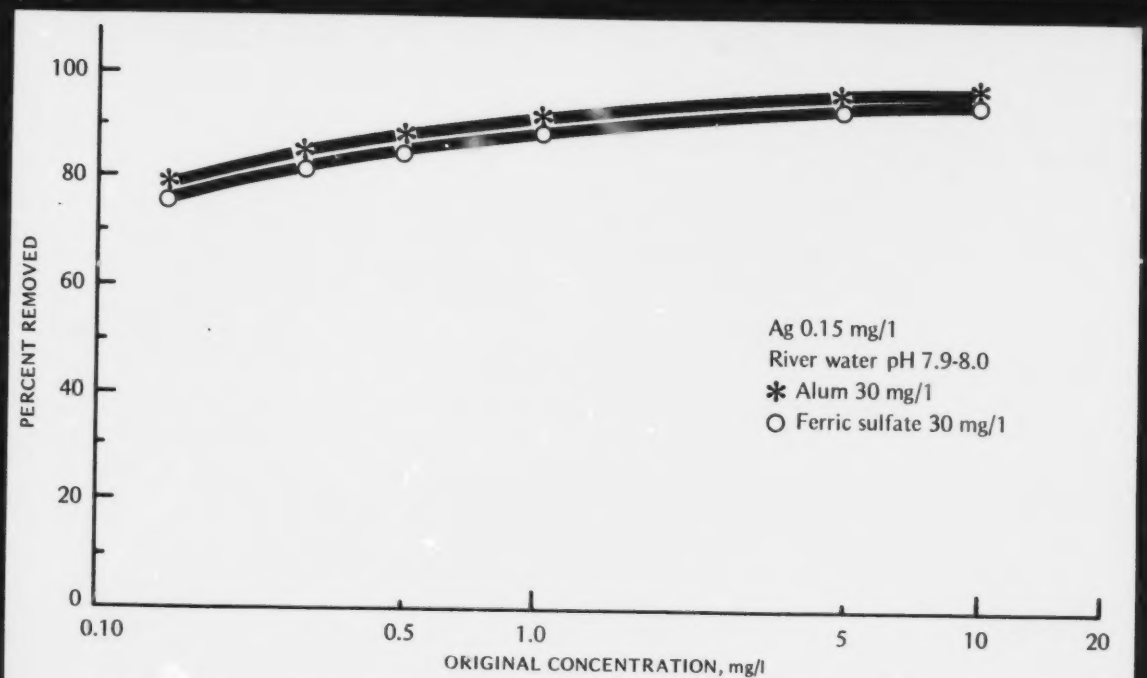


FIGURE 34 SILVER REMOVAL BY ALUM AND IRON COAGULATION (1)

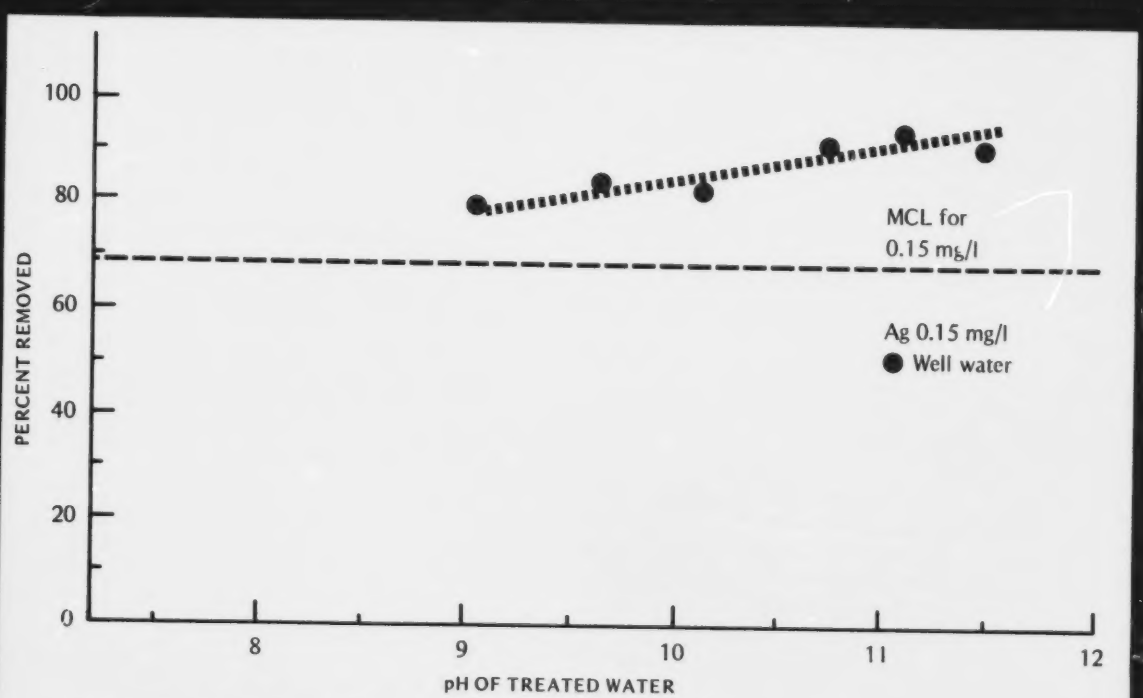


FIGURE 35 SILVER REMOVAL BY LIME SOFTENING (1)

Treatment Costs for the Removal of Inorganic Contaminants

The cost of reducing a contaminant or several contaminants below the MCL's will depend on the required treatment technique and on whether a treatment facility exists. Modifications to or changes in operation of an existing plant may result in only a slight operating cost increase, or possibly no additional cost at all. On the other hand, if there is no treatment facility, the cost will be the expense of constructing and operating a new treatment plant.

As indicated in the Introduction, the information contained herein is general and should be used only as a guide. Therefore, the reader is cautioned once again that these data are intended for planning and not for design purposes. Material and labor costs vary from location to location and change almost daily. The exact cost can only be determined by costing out a specific plant according to the economic factors of the location. In the final analysis, the actual cost could be considerably different from that presented in the following sections.

COST OF MODIFICATIONS OR OPERATIONAL CHANGES AT EXISTING TREATMENT PLANTS

The foregoing information on the removal of specific contaminants by conventional treatment techniques showed that removals depend on various operational parameters such as pH, coagulant, coagulant dose, and valence of the contaminant. A change in any one of these operational variables to achieve optimum removal of the contaminant should result in only a very slight increase in operating cost of no more than a cent or two per 1,000 gallons of water treated.

If an existing plant must be modified to provide an additional treatment step or two, or if new equipment must be purchased, the cost will be higher than that resulting from only an operational change. Although some capital costs will occur, the increase in operating cost should not be more than a cent or two. It is not practical to list capital costs for all potential modifications, and this document will omit them.

COST OF NEW TREATMENT FACILITIES

Although no one treatment method is effective for the removal of all inorganic contaminants, some grouping can be made. For example, lime softening is a good technique for the removal of lead, cadmium, Cr^{+3}, As^{+5}, and silver. Treatment costs for the removal of these contaminants by lime softening, therefore, should be approximately the same. For the sake of simplicity and to avoid repetition, treatment cost information presented is based on treatment technique rather than on individual contaminant.

David Volkert and Associates prepared a report entitled "Monograph of the Effectiveness and Cost of Water Treatment Processes for the Removal of Specific Contaminants" for EPA (1). This report provides cost information on specific water treatment processes based on economic indexes of July 1973. Water and Air Research, Inc., updated some of this information to October 1975 for use in a report for EPA entitled "Cost Calculations Procedures for Determination of Costs of Radium Removal from Potable Water Supplies" (2). The following cost information on new treatment facilities has been developed primarily from these two reports. The reader is again reminded that these cost data are intended as a guide for general planning estimates and should not be used for design purposes.

Capital and operating cost information on reverse osmosis, ion exchange, and lime softening are shown in figures 36 and 37. A band is shown for ion exchange and lime softening. This band represents the cost of softening about 80 percent of the total water flow having a total dissolved solids (TDS) range of 2,000-4,000 and 150-750 (as $CaCO_3$). A single line is shown for reverse osmosis because the capacity of the unit does not vary with the TDS or hardness of the water. The reverse osmosis costs are also based on the

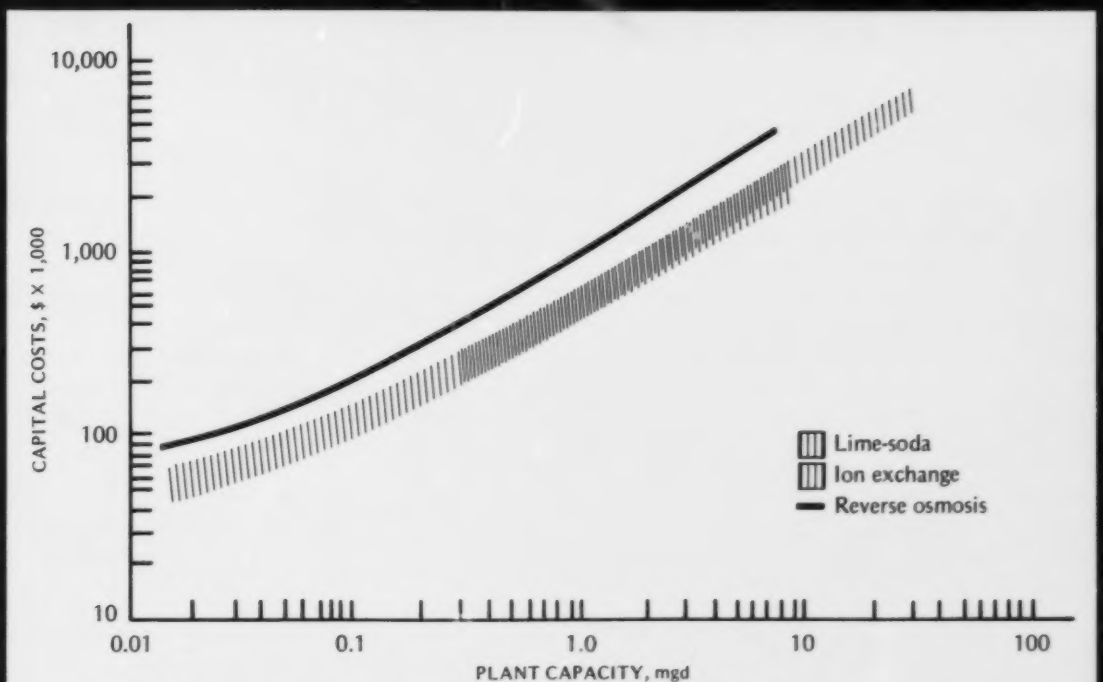


FIGURE 36 CAPITAL COSTS OF WATER TREATMENT PLANTS

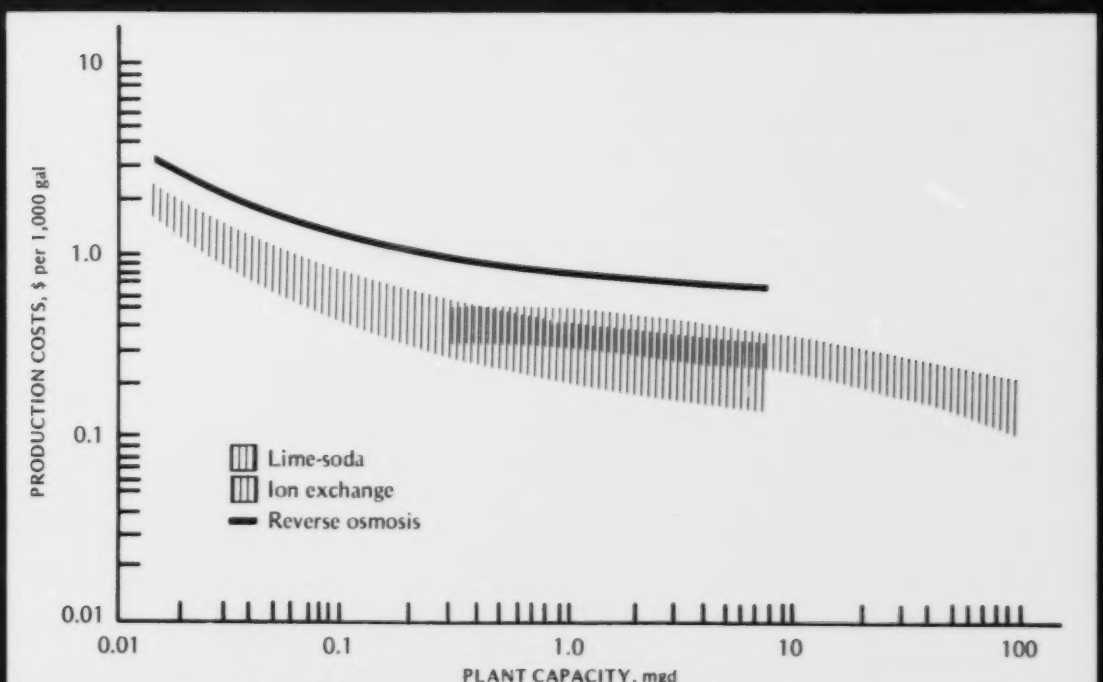


FIGURE 37 ANNUAL PRODUCTION COSTS: OPERATION, MAINTENANCE, AMORTIZATION

treatment of about 80 percent of the total flow. The cost elements included in the capital and operating costs figures are shown in table 4.

The costs for chemical coagulation treatment are about the same as those for lime softening because the unit processes are almost identical. Lime softening costs can therefore be used for chemical coagulation treatment cost estimates. The operating cost will be somewhat conservative because lime softening generally uses more chemicals and requires additional pH adjustment equipment.

TABLE 4. Elements Included in Capital and Operating Costs

Capital cost elements	Construction for site preparation
	Plant construction
	Land costs, assumed at $1,850 per acre
	Interest during construction, 8 percent
	Startup cost
	Owners general expense, 12 percent of construction
Operating cost	Chemicals
	Labor
	Operation and maintenance
	Amortization at 7-percent compound interest for depreciating capital
Useful life:	
Lime-soda plants	40 years
Ion exchange	20 years
Reverse osmosis	20 years

REFERENCES

1. *Monograph of the Effectiveness and Cost of Water Treatment Processes for the Removal of Specific Contaminants.* Vol. I, *Technical Manual.* Contract No. 68-01-1833. U.S. Environmental Protection Agency, Washington, D.C., 1974. 324 pp.
2. Cost Calculations Procedures for Determination of Costs of Radium Removal from Potable Water Supplies. Contract No. 803854-01. U.S. Environmental Protection Agency, Cincinnati, Ohio, 1976.

Treatment Techniques for the Removal of Turbidity from Drinking Water

by GARY S. LOGSDON
Water Supply Research Division, MERL
U.S. Environmental Protection Agency
Cincinnati, Ohio

A maximum contaminant limit (MCL) has been established for turbidity because certain types of turbidity-causing solids, such as organic matter, can interfere with disinfection or microbiological determinations, or can prevent maintenance of an effective disinfectant agent throughout the distribution system (1). Suspended solids that cause turbidity can be removed from water by coagulation, sedimentation, and filtration. In addition to preparing the raw water for disinfection, sedimentation and filtration offer some fringe benefits. Very clear waters are more esthetically appealing to consumers. Suspended matter removed by filtration cannot settle in dead ends in the distribution system and cause problems with chlorine demand, microbiological growths, or taste and odor. Also, removal of suspended matter can result in removal of contaminants—for example, heavy metals, pesticides, and asbestos-adsorbed or attached to the suspended matter. Sedimentation and filtration can also remove precursor substances that could form trihalomethanes upon free residual chlorination.

The MCL's for turbidity apply to both community and noncommunity water systems using surface water sources in whole or in part. The MCL's for turbidity in drinking water, measured at representative entry points to the distribution system, are:

(a) One turbidity unit (TU), as determined by a monthly average pursuant to § 141.22, except that five or fewer turbidity units may be allowed if the supplier of water can demonstrate to the State that the higher turbidity does not do any of the following:
  (1) Interfere with disinfection;
  (2) Prevent maintenance of an effective disinfectant agent throughout the distribution system; or
  (3) Interfere with microbiological determinations.

(b) Five turbidity units based on an average for two consecutive days pursuant to § 141.22.

The MCL for turbidity is 1 tu, but under certain circumstances it can be 5 tu. It is assumed for this document that filtration plants will have an operating goal of producing water meeting the 1-tu limit, or better if possible.

The MCL for turbidity applies to systems treating surface sources in whole or in part. Therefore, it is not the purpose of this document to discuss clarification of ground waters to remove iron or manganese.

Filtration as a water treatment process has been studied and applied on a municipal scale for many years in the United States. Granular media filtration with sand filters was thoroughly researched by Fuller at Louisville at the turn of the century and has since been investigated and used at many locations in the United States. Mixed media filtration was pioneered by Conley and Pitman at Hanford after World War II. The use of dual media has been generally recognized as superior to single media filtration (2). Direct filtration, or filtration of water after chemical conditioning but without settling, was attempted before the turn of the century in the early days of filtration. This process has been developed rationally and applied effectively in a gradual fashion since World War II.

During World War II filter-aid filtration (diatomaceous earth (DE) filtration) was developed for potable water use by the U.S. Army Corps of Engineers. Diatomaceous earth filtration has been used for municipal water treatment since the 1950's and is an alternative to granular media filtration.

Treatment Techniques

Both granular media and DE filtration can be used to filter water and produce an effluent that meets the MCL for turbidity. The nature and amount of

treatment before filtration and the choice of granular media or DE filters should be made case by case, considering factors such as raw water quality, quality fluctuations, plant size, and area available for plant construction.

Because of the many papers, articles, symposia, and books on filtration, a complete bibliography would be virtually impossible. Two works that should be mentioned, however, are *Water Quality and Treatment* (2) and *Water Treatment Plant Design* (3), both published by the American Water Works Association (AWWA). In addition, papers on filtration are often found in the monthly issues of the *Journal of the American Water Works Association.*

GRANULAR MEDIA FILTRATION

Most granular media filters are operated as gravity filters, open to the atmosphere. Some are operated inside closed vessels as pressure filters. The quality and kind of pretreatment before filtration is determined by factors such as raw water turbidity, filtration rate, and media size rather than by whether the pressure or gravity mode is used. Pressure filters would seldom have trouble with air binding, but other granular media filtration problems, such as mud balls or media upset, could occur. One disadvantage of pressure filters is that the operator cannot see the media and recognize symptoms of filter operating or backwashing problems. Pressure filters are often used when raw water is supplied under pressure, and is filtered and delivered to the distribution system without repumping—which is not often done with surface waters.

Two key factors in successful operation of granular media filters are proper conditioning of the water before filtration and thorough backwashing of media at the end of each run. Variables affecting floc strength and completeness of flocculation are rapid mix time and energy (velocity gradient (G) in feet per second per foot), flocculation time and energy, and inorganic chemicals or polymers and doses used. Conditioning chemicals are nearly always needed for effective turbidity removal by granular media filtration.

The complex interrelationships between these variables are best understood through pilot plant tests or careful observation of treatment plant performance during varying conditions of raw water quality and treatment techniques. With proper pretreatment, including rapid mix and/or flocculation, the operator should be able to condition floc to be strong enough to be retained in the media but not so strong as to accumulate at the media-water interface in dual or mixed media filters in the direct filtration process. At plants having settling, floc should be properly conditioned so that it will settle well but not penetrate the filters if it does carry over from the settling basin. The purpose of settling is to prepare a turbid water for effective, cost-efficient filtration.

Continuous monitoring of filtered water turbidity has been recommended by Culp (4). While settling and filtration processes can be monitored by using laboratory turbidimeters to measure discrete samples, continuous turbidimeters with recorders (which cost under $1,000) provide the plant operator with a positive, continuous record of the filtered water turbidity.

For continued, effective filter operation, adequate backwashing is a must. Poor backwash techniques may not impair filter performance immediately. Eventually, however, such problems as mud balls, sand boils, and pulling away from sidewalls can occur. Filter media must be cleaned thoroughly. Often surface wash is used to augment the backwash action and break up tougher floc in the media. Floc containing polymer seems more difficult to wash out of filters than floc from inorganic coagulants. In some instances air-assisted wash has been used to remove polymer floc.

DIATOMACEOUS EARTH FILTRATION

Because water is seldom, if ever, preconditioned at DE filter plants, the principal operating variables relate to the filter precoat and body feed during the filter run. Both the DE particle size and amount (pounds per square foot for precoat and milligrams per liter for body feed) of DE used can be varied according to filter design and raw water quality. The operator's goal is to use a grade of DE fine enough to yield acceptable filtered turbidity, while applying enough body feed for a long filter run and, thus, for an economical use of precoat. Insufficient body feed causes filter blinding and short, uneconomical runs that waste precoat filter aid.

Backwashing of diatomite filters also should be thorough. All of the used filter cake should be removed, and the septum should be cleaned thoroughly so that the new precoat will readily form on it. Backwashing techniques for diatomite filters vary, depending on the type of equipment and the manufacturer.

Disposal of Filter Plant Sludge

The complexity of water plant waste treatment and disposal is so great that it cannot be dealt with in this document; however, water utility operators should be aware that, in the future, water plant wastes will be considered pollutants, and will require environmentally acceptable disposal methods. Because sludge characteristics vary from plant to plant and from process to process, the characteristics of the waste material should be determined before treatment and disposal methods are formulated for a given plant. In general, bec use most water filtration plant wastes have a high water content, they are usually dewatered before ultimate disposal is undertaken. Dewatering techniques that could be used for sludge treatment include sand drying beds, lagoons, thickeners, centrifuges, vacuum filters, pressure filters, and natural freezing. Under certain circumstances, municipal water plant sludge can be discharged to the sanitary sewer and treated at the sewage treatment plant. Generally, the most acceptable site for ultimate disposal of dewatered sludge is on land.

Treatment Costs for Turbidity Removal

At existing filtration plants, costs for meeting the MCL for turbidity might include increased operator diligence, more frequent (perhaps continuous) turbidity monitoring, slightly higher doses of chemicals, or a different grade of DE body feed. For example, existing granular media plants might begin to use small amounts of polymer in addition to inorganic coagulants. Or diatomite plants might switch to finer sizes of precoat and body feed filter aid, and perhaps use a slightly higher body feed dose, to attain the desired clarity in the filter effluent. Costs for these operational changes should be less than 1 cent per 1,000 gallons.

At some plants it might be necessary to convert rapid sand filters to dual media or mixed media filters. In addition to filter media, costs that might be associated with filter conversion would be costs for improved backwash capability. Additional information on this subject can be found in AWWA's *Proceedings of the 1974 Seminar on Upgrading Existing Water Treatment Plants* (5).

Costs for plant upgrading are not easily predicted, because local circumstances can be so varied. Hudson's paper, "Plant Up-Rating Case Studies," is informative on this topic (6). Hudson states that some plants are designed for uprating, some are not, and still others are difficult or impossible to uprate. Hudson's work deals with increasing plant production by modifying the plant. This approach is probably more expensive than making modifications to improve effluent quality. Nevertheless, the individualized approach to each plant is the type of technique that would be needed in modifying a plant to improve water quality. Plant modifications made for the dual purposes of improved quality and higher production rate should be expected to be more costly.

For plants having raw water of such good quality that filtration is not practiced now but will be required in the future because the turbidity MCL will be a primary, or mandatory, standard, direct filtration with granular media or DE should almost certainly be sufficient. Costs for treatment plant construction and for operation and maintenance have been reviewed and estimates can be made. Capital cost curves are included for four kinds of plants—granular media plants built by conventional construction (fig. 38), direct filtration plants (fig. 39), granular media package plants (fig. 40), and DE filter plants (fig. 41).

Costs for conventionally built granular media and DE filter plants were obtained and updated to December 1975, using EPA's Sewage Treatment Plant Construction Cost Index. Cost data are identified as construction costs or estimated costs. For granular media, data are also identified as for direct filtration plants, plants with 1-hour contact basins, and plants with settling basins. Costs along the upper line on cost curves should be more typical of totally new plants requiring intakes and raw water pumping, or filtering at 2-3 gal/min/ft^2. Costs on the lower curve would be more typical of adding a filter plant to an existing water system, or filtering at 5-6 gal/min/ft^2.

Costs for package plants are based on doubling package plant equipment cost to account for installed cost and adding the cost of a tank to serve as a clearwell. The concrete tank size was equal to 4 hours' filter plant production. Concrete tank costs were estimated using "Cost Aspects of Water Supply" (7).

Costs for operation and maintenance of filter plants are not easily obtained, and available data show a broad range of costs, probably because of the various methods of cost allocation and accounting used by different utilities. Costs suggested for inclusion in treatment operation and maintenance in this report are those for raw water acquisition, chemicals, labor, electricity and utilities at the treatment plant, and maintenance. Costs of high service pumping or meter repair shop operation were considered distribution costs, even if incurred at the filtration plant.

Operation and maintenance costs for granular media filtration range from 4 cents to 8 cents per 1,000 gallons of water treated. Operation and maintenance costs for DE filtration range from 4 cents to 15 cents per 1,000 gallons treated. Because of the small number of plants providing data for operation and maintenance costs, no assurance exists that these costs are representative of most plants or that the cost range is all inclusive. Annual costs, including capital plus operating and maintenance data, are shown in figure 42.

These cost data are presented to give examples of the nature of costs associated with water filtration. For a cost estimate to have value and to be usable at a specific site, it must be prepared for the locality considered. Costs of capital, chemicals, material, supplies, energy, and labor vary greatly and can influence the choice of treatment selected.

References

1. Symons, J. M., and J. C. Hoff. Rationale for Turbidity Maximum Contaminant Level. In: *Proceedings of the Third Water Quality Technology Conference*, American Water Works Association, Atlanta, Ga., Dec. 8-10, 1975.
2. American Water Works Association. *Water Quality and Treatment.* 3rd ed. McGraw-Hill, New York, N.Y., 1971.
3. American Water Works Association, American Society of Chemical Engineers, and Conference of State Sanitary Engineers. *Water Treatment Plant Design.* American Water Works Association, Denver, Colo., 1969.
4. Culp, R. L. Direct Filtration. Presented at California Section, American Water Works Association. Water Treatment Forums V and VI, Oakland and Los Angeles, Calif., Sept. 14, 15, 1976.
5. *Proceedings of the 1974 Seminar on Upgrading Existing Water Treatment Plants.* American Water Works Association, Denver, Colo., 1974.
6. Hudson, H. E., Jr. Plant Up-Rating Case Studies. In: *Up-Grading Existing Water Treatment Plants.* American Water Works Association, Denver, Colo., 1974.
7. Cost Aspects of Water Supply. In: *Proceedings of the Eighth Annual Sanitary Engineering Conference.* University of Illinois, 1966.

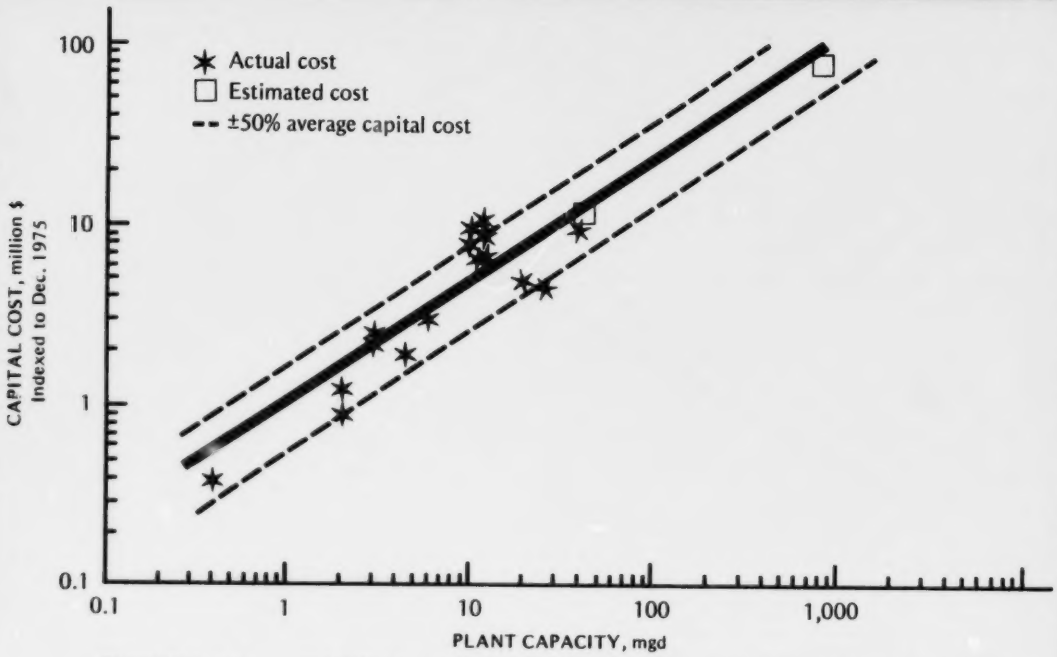


FIGURE 38 CAPITAL COST OF GRANULAR MEDIA PLANTS WITH SETTLING

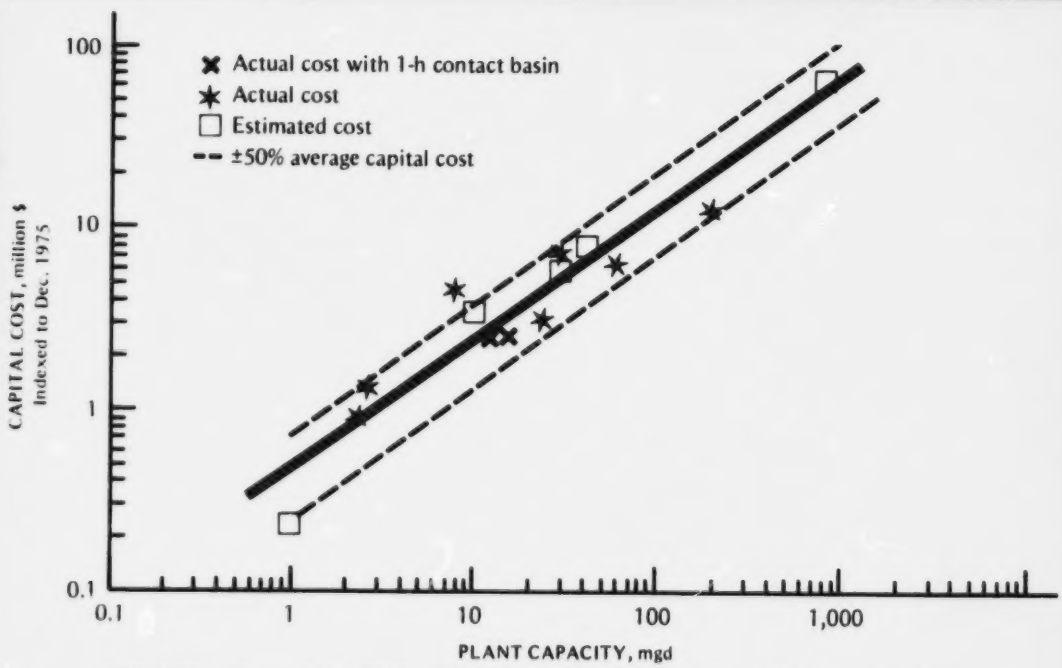


FIGURE 39 CAPITAL COST OF GRANULAR MEDIA, DIRECT FILTRATION PLANTS

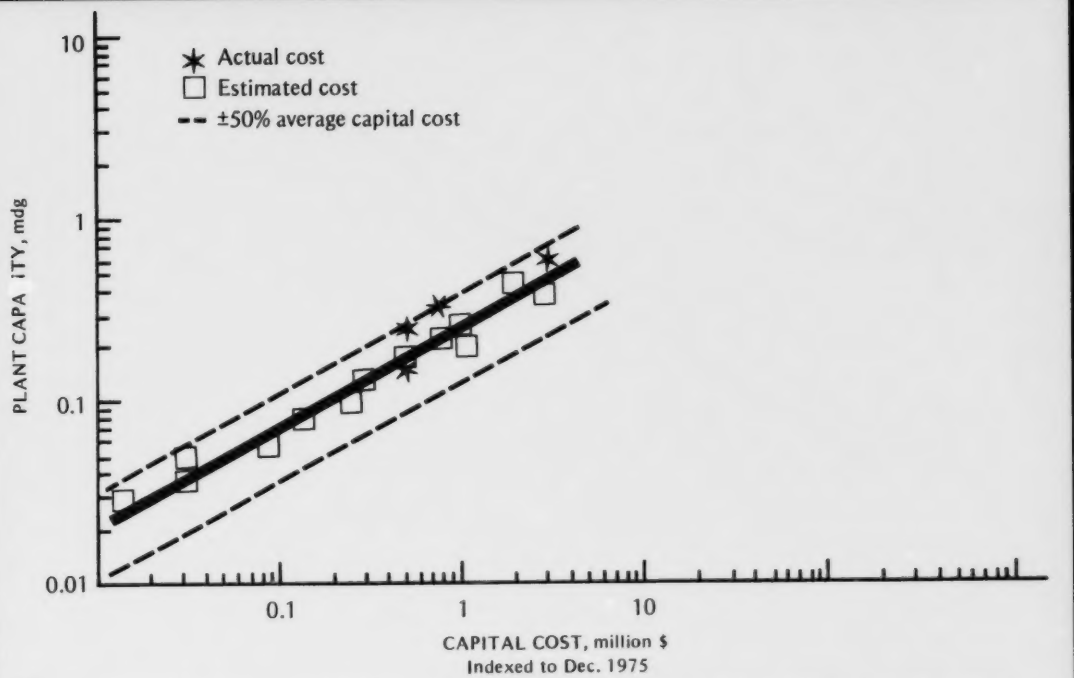


FIGURE 40 CAPITAL COST OF GRANULAR MEDIA PACKAGE PLANTS, INSTALLED, INCLUDING CLEARWELL

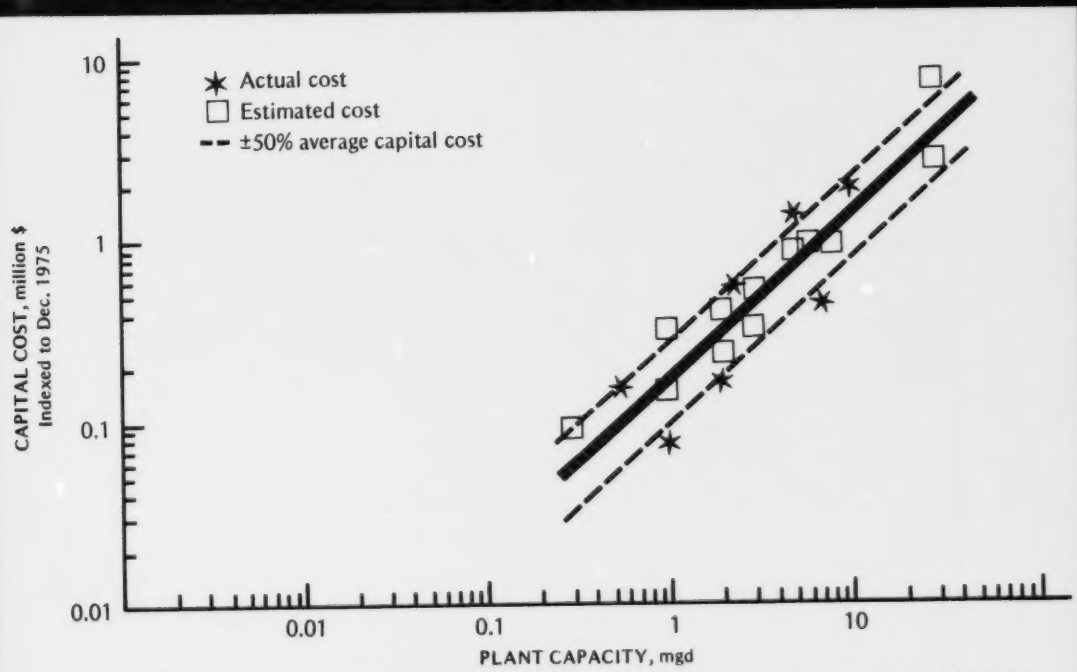


FIGURE 41 CAPITAL COST OF DIATOMACEOUS EARTH FILTRATION PLANTS

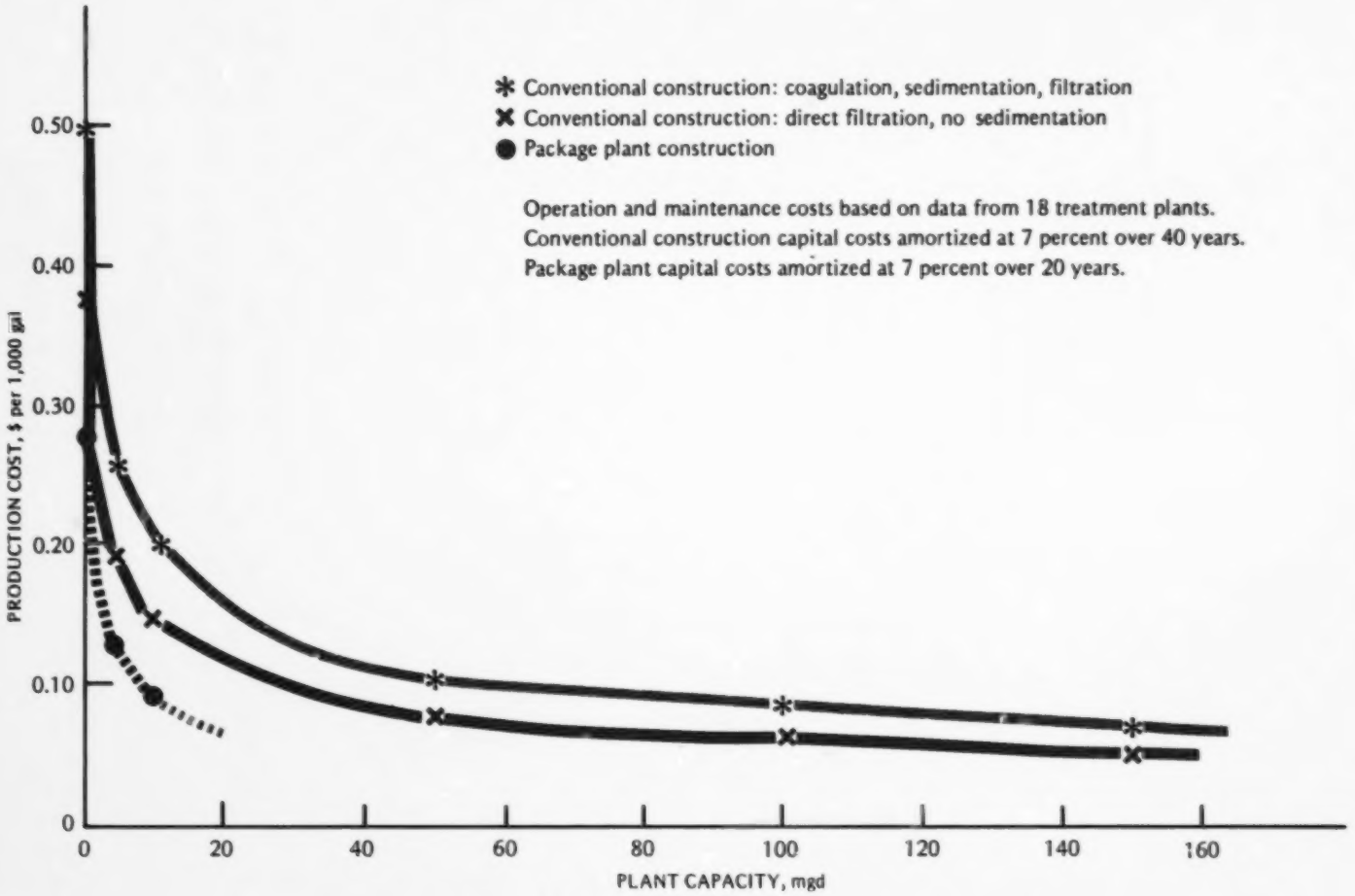


FIGURE 42 TOTAL COST OF WATER PRODUCTION VERSUS PLANT CAPACITY

Treatment Techniques for the Removal of Coliform Organisms from Drinking Water

by GARY S. LOGSDON
Water Supply Research Division, MERL
U.S. Environmental Protection Agency
Cincinnati, Ohio

Modern water treatment generally includes a process of disinfection designed to kill microbiological pathogens. Although a number of disease-causing micro-organisms exist, their detection and identification is difficult and tedious. Therefore, the efficacy of the disinfection process is generally not measured by tests for the absence of pathogens but by measuring a group of indicator micro-organisms, the coliform group of bacteria. Because coliforms originate primarily from the intestinal tract of warm-blooded animals, including humans, they are indicators of possible fecal contamination.

Certain pathogenic micro-organisms, particularly cysts, are more resistant to disinfection than are coliform bacteria. If a water is known or likely to be contaminated by cysts of *Endamoeba hystolytica* and *Giardia lamblia*, the treatment process should include disinfection and either diatomaceous earth filtration or coagulation and granular media filtration.

Maximum Contaminant Levels (MCL's)

The MCL's for coliform bacteria, applicable to community and noncommunity water systems, are as follows (1):

(a) When the membrane filter technique pursuant to § 141.21(a) is used, the number of coliform bacteria shall not exceed any of the following:
  (1) One per 100 milliliters as the arithmetic mean of all samples examined per month pursuant to § 141.21(b) or (c);
  (2) Four per 100 milliliters in more than one sample when less than 20 are examined per month; or
  (3) Four per 100 milliliters in more than five percent of the samples when 20 or more are examined per month.

(b) (1) When the fermentation tube method and 10 milliliter standard portions pursuant to § 141.21(a) are used, coliform bacteria shall not be present in any of the following:
  (i) more than 10 percent of the portions in any month pursuant to § 141.21(b) or (c);
  (ii) three or more portions in more than one sample when less than 20 samples are examined per month; or
  (iii) three or more portions in more than five percent of the samples when 20 or more samples are examined per month.

  (2) When the fermentation tube method and 100 milliliter standard portions pursuant to § 141.21(a) are used, coliform bacteria shall not be present in any of the following:
  (i) more than 60 percent of the portions in any month pursuant to § 141.21(b) or (c);
  (ii) five portions in more than one sample when less than five samples are examined per month; or
  (iii) five portions in more than 20 percent of the samples when five or more samples are examined per month.

(c) For community or non-community systems that are required to sample at a rate of less than 4 per month, compliance with paragraphs (a), (b)(1), or (b)(2) of this section shall be based upon sampling during a 3-month period, except that, at the discretion of the State, compliance may be based upon sampling during a one-month period.

Disinfection of Water

The methods by which water can be disinfected include the use of chlorine, ozone, and chlorine dioxide. Other methods not as practical or not generally used for the treatment of drinking water, and therefore not discussed in this document, include gamma radiation, heat, silver, and ultraviolet light.

TURBIDITY

Disinfection efficacy is related to the clarity of the water being treated. Disinfection of very turbid waters can be difficult or impractical; therefore, in the production of potable waters from turbid surface sources, coagulation, flocculation, sedimentation, and filtration are used to present a barrier to the passage of micro-organisms into the water distribution system and to produce water that is more easily disinfected. It has been shown that sedimentation and filtration of properly conditioned waters can remove a significant part of the micro-organisms present. These processes are not totally effective, however, so they must be followed by disinfection. Disinfection is more effective when the water is of high quality. Therefore, the turbidity limit in the Drinking Water Regulations (1) is 1 tu under most circumstances. Treatment methods for producing adequately clarified drinking water are discussed earlier in the section on turbidity.

DISINFECTION BYPRODUCTS

In recent years, methods for detecting organic compounds in water have been substantially improved, and small quantities of organic compounds that were previously undetectable can now be measured. This improvement in analytical capabilities has resulted in the discovery of organic byproducts arising from the process of chlorine disinfection, some of which may be hazardous to human health (2-8).

Research is still being conducted to further the understanding of the problem of chlorination byproducts. In general, however, the potential for the formation of chlorination byproducts should be recognized and minimized where possible. One method of reducing chlorination byproducts is to add the chlorine to water with the highest possible quality. Some treatment before chlorination generally reduces the amount of chlorination byproducts. The microbiological quality of the water is of prime importance, however, and changes in treatment practice must not result in a deterioration of the microbiological quality of the finished drinking water.

CHLORINATION

Much of the material in this section was drawn from a chapter in *Water Quality and Treatment* by E. J. Laubusch (9). For a more thorough review of disinfection refer to this work, which provides a bibliography of 207 entries.

The first continuous application of chlorination to a municipal water supply was at the Boonton Reservoir of the Jersey City Water Works in 1908. Since that time, chlorination has become widely accepted, and currently most water utilities use chlorine for disinfection.

Chlorination may be accomplished using gaseous chlorine or hypochlorite. Liquid chlorine is the least expensive form of chlorine and is especially suitable for larger water utilities. For small utilities, hypochlorite can be added to the water by means of a solution feed pump. For a ground water source, a convenient means of hypochlorite feed is to have the solution feed pump operating simultaneously with the well pump.

The ability of chlorine to kill micro-organisms is related directly to the chlorine concentration and contact time, other factors being equal. Low chlorine concentrations require longer contact time to achieve equivalent kill. Other factors are its form (combined (with ammonia) versus free chlorine), temperature, and pH of the water. Free chlorine is a much more effective disinfectant than combined chlorine (see fig. 43) (10). Combined chlorine (chloramines) can persist longer in some distribution systems because they are less reactive. Some water utilities have had success controlling bacterial aftergrowth in distribution systems using combined chlorine residuals.

The disinfecting efficiency of free available chlorine residual decreases significantly as pH rises (10). The chemistry of chlorination of pure water is briefly summarized, as follows:

$$Cl_2 + H_2O \rightarrow H^{+1} + Cl + HOCl$$

$$HOCl \rightleftarrows H^{+1} + OCl^{-1}$$

Chlorination of pure water causes the formation of hypochlorous acid (HOCl), which dissociates to form the hypochlorite ion (OCl^{-1}). Hypochlorite ion is a

relatively poor disinfectant. The distribution of HOCl and OCl^{-1} at different pH values is shown in figure 44 (11). The concentration of titratable free available chlorine needed to obtain 99-percent *E. coli* kill in 30 minutes is shown as a function of pH in figure 45 (10). Chlorine is a less effective disinfectant at high pH than at low pH. It has been demonstrated that the excess lime softening process has disinfecting capabilities (12). Riehl listed three factors important in lime sterilization:

- Quantity of excess lime used
- Time of reaction
- Amount of particulates, organics, and microorganisms in water

Fair, Geyer, and Okun (11) state that pathogens do not survive long at pH values above 11. The reduced efficiency of chlorine at high pH may be compensated for by the bactericidal effect of high pH in the excess lime softening process. At plants using this process it would be prudent to evaluate the disinfection effect of excess lime softening when any changes in the disinfection process are considered.

In many water utilities that chlorinate to produce a free residual, observation of plots of chlorine residual versus applied chlorine shows that the chlorine residual increases, then decreases, and finally increases again. Such a curve is shown in figure 46 (13) and is termed a breakpoint curve. Research results from a number of laboratories have shown that the breakpoint phenomenon is related to the chemistry of chlorine and nitrogen compounds. Ammonia, when chlorinated, forms chloramines that are subsequently destroyed in the breakpoint chlorination process.

Viewing breakpoint chlorination as the relationship between water, chlorine, and nitrogen compounds has provided a useful theory for laboratory work, but it is probably too simplistic when we consider what actually happens in water treatment plants. White reported that Griffin found tastes and odors that occurred at chlorine doses below the breakpoint to disappear above the breakpoint (10). This finding suggests the possible involvement of substances other than chlorine and ammonia nitrogen.

The concept of "destroying" compounds in breakpoint chlorination was mentioned by Cox (13), and White referred to "disappearance" of tastes and odors. It is vital to remember that matter is neither created nor destroyed; it merely changes form. White shows that an end product of ammonia chlorination is nitrogen gas. Nitrogen gas may escape from the water, but nitrogen atoms have not been destroyed. This matter is of practical importance—not just theoretical concern—because of the possibility that organic compounds could react with chlorine before the breakpoint is reached. The disappearance of tastes and odors hints at this phenomenon. There is no assurance at present that breakpoint chlorination will destroy undesirable organics, or that chlorinating less than to the breakpoint will assure a water free of hazardous chlorinated organic compounds.

OZONE

Ozone has been used as a disinfectant since about 1900, primarily in Europe and Canada. Because few water utilities in the United States now use ozone, information on ozonation practices is based mostly on foreign experience.

Ozone is reported to be a more effective disinfectant than chlorine, and it is effective over a wider range of pH and temperature. Ozone can be used in lower doses than chlorine to achieve equivalent disinfectant kill, and it is effective in reducing or eliminating tastes and odors. Ozonation does not cause the formation of trihalomethanes (THM's) during disinfection. Water that has been disinfected with ozone, however, may form THM's if chlorine is applied to provide a free chlorine residual in the distribution system. Disinfection-level ozone doses do little to remove THM precursor (8).

Use of ozone as a disinfectant has had a number of disadvantages in the past, but a number of these are being overcome. Laubusch (9) indicated that ozonation energy requirements and operating costs were higher, "about 10 to 75 times higher than chlorine." Laubusch also indicated that analytical methods were not sufficiently specific or sensitive for effective process control. Both of these observations are no longer true. Ozonation costs are compared with chlorination costs in the cost section of this document, and they are similar. Closed-loop instrumentation for ozonation control in wastewater treatment has now been developed and marketed.

Ozone must be generated on site because it is highly reactive and thus cannot be shipped as chlorine can. Ozone also decomposes very rapidly after generation. Its half-life in water is approximately 20 minutes or less. In plants big enough to produce ozone from pure oxygen economically, ozone production is not difficult. Small plants usually produce ozone from air that has been dried by refrigeration.

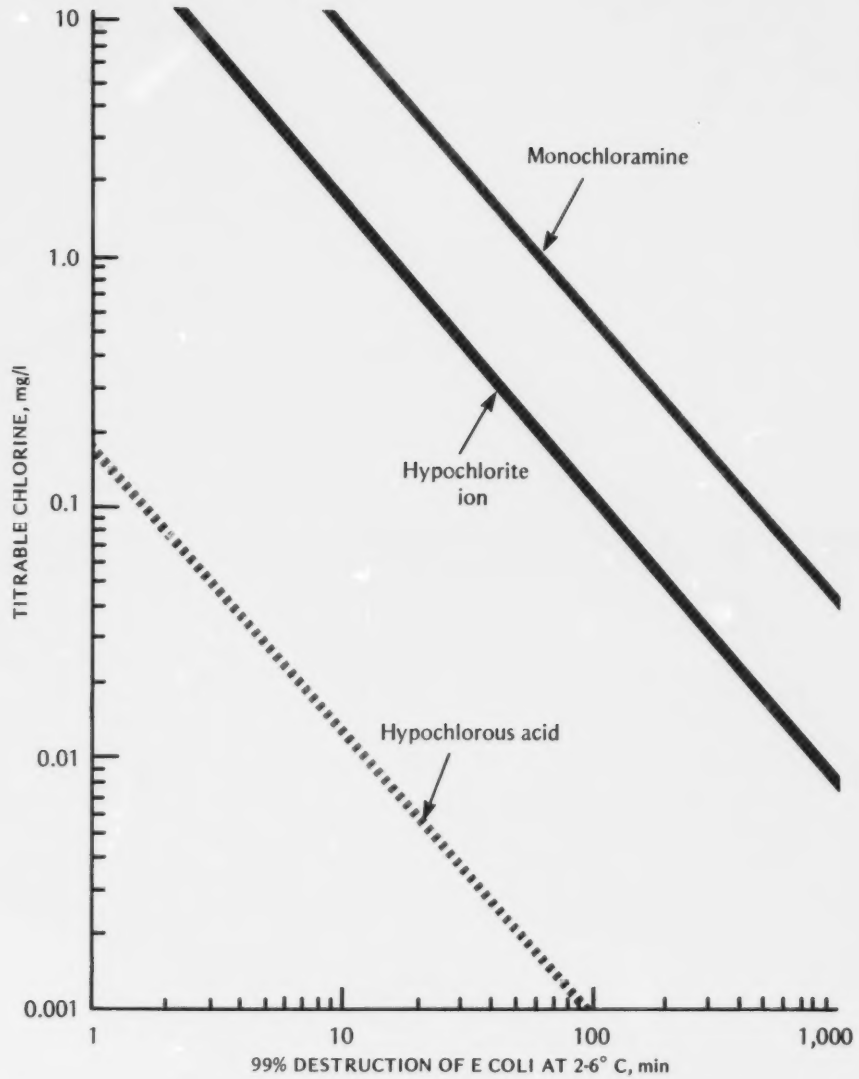


FIGURE 43 COMPARISON OF GERMICIDAL EFFICIENCY OF HYPOCHLOROUS ACID, HYPOCHLORITE ION, AND MONOCHLORAMINE (10)

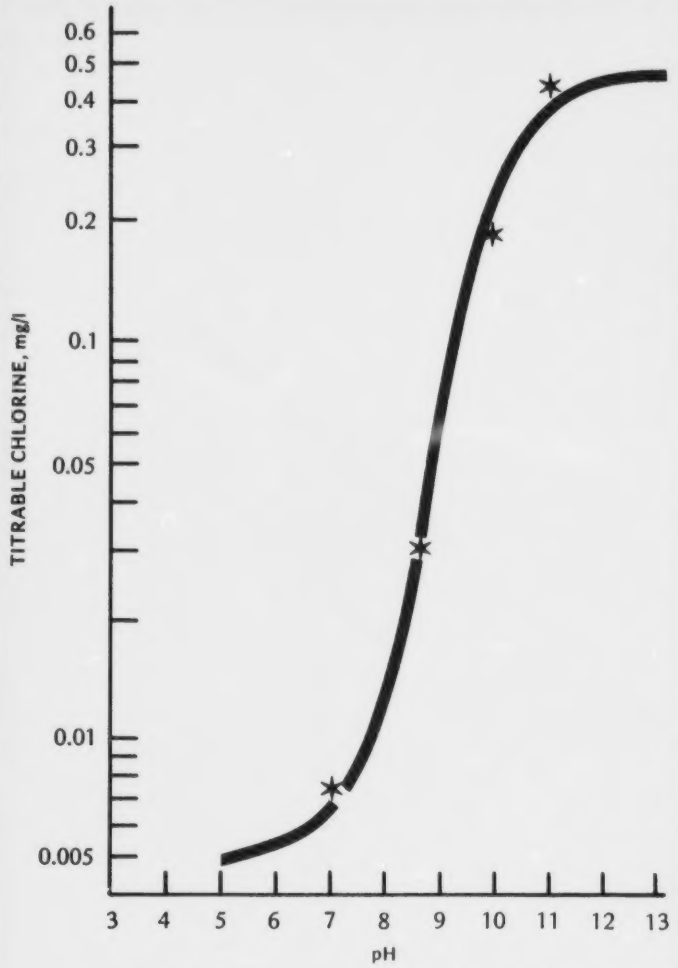


FIGURE 45 RELATIVE GERMICIDAL EFFICIENCY OF HYPOCHLOROUS ACID AND HYPOCHLORITE ION (10)

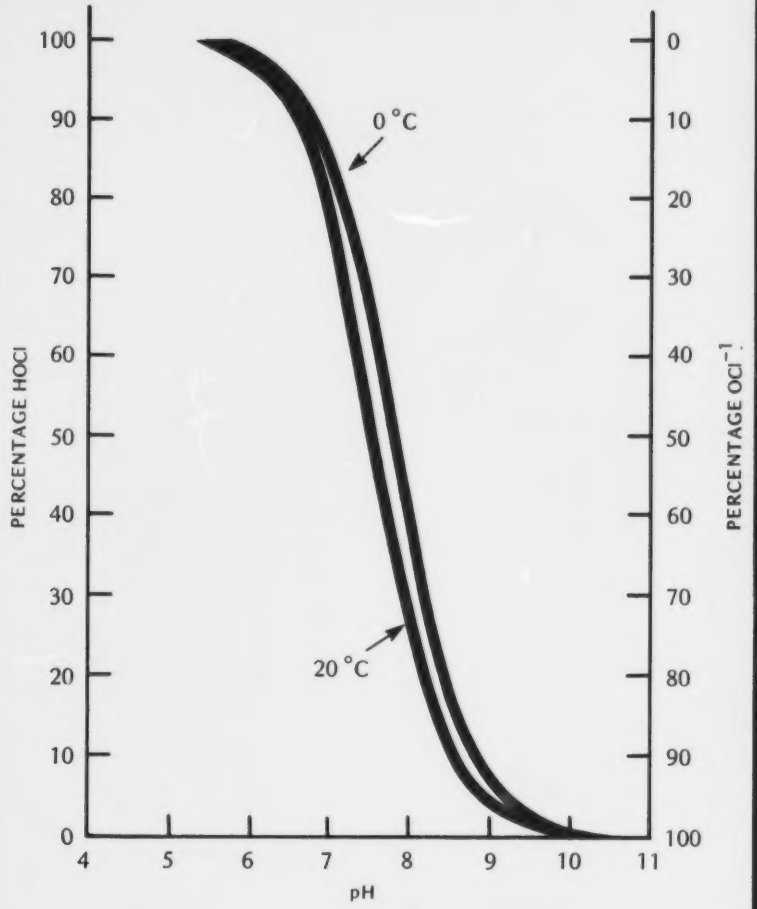


FIGURE 44 DISTRIBUTION OF HYPOCHLOROUS ACID AND HYPOCHLORITE ION IN WATER AT DIFFERENT pH VALUES AND TEMPERATURES (11)

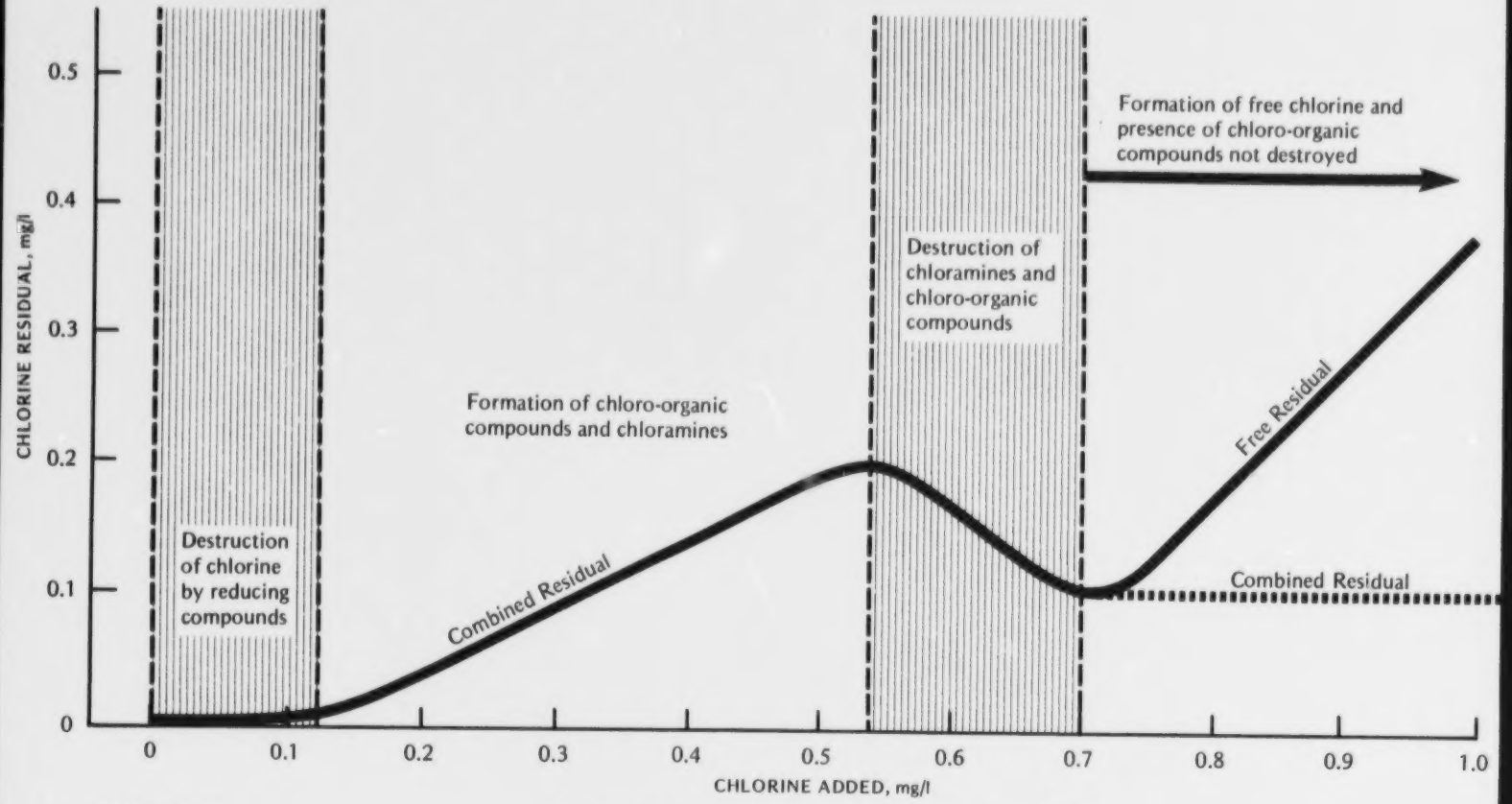


FIGURE 46 REACTIONS OF CHLORINE IN WATER (13)

Because ozone is a gas and is not highly soluble in water, ozonation facilities differ from chlorination facilities. The use of tall columns and special diffusers to maximize ozone-water contact is common. Ozone contact is often done in various proprietary devices. Multiple-contact stages may also be used. Ozone application facilities and technology probably have more in common with pure oxygen activated sludge technology than with ordinary water treatment facilities. Ozone treatment still has some disadvantages, including the lack of ozonation experience in the American water utility industry and an associated tendency to favor the use of the old, familiar disinfectant, chlorine.

There are other disadvantages, including the lack of ozone residual in the distribution system, difficulty in operating ozonators at varying rates to match water production and ozone demand, complicated equipment needed for drying air at plants too small to use pure oxygen, and the lack of data on the organic byproducts of ozonated raw waters. The organic oxidation products problem is not limited to ozonation of raw water, but may occur if ozone is applied to settled or finished water. Regrowth is another disadvantage of using ozone without a residual in the distribution system.

Some problems associated with ozonation may be solved more readily than others. For example, installation of modular ozonators might permit variable ozone production by starting or stopping individual units. One of the more serious considerations in treating water with ozone is the question of oxidation product formation. It has been shown that ozone appled at disinfection-level doses does not eliminate the total organic carbon content of water. Thus, even though chlorine or chlorine dioxide could be used to maintain a distribution system residual, THM production could occur with the use of free chlorine or with the use of excess chlorine in chlorine dioxide production. Further research is needed to resolve this question.

Based on current knowledge about ozone as a water disinfectant, its use could be considered seriously by water utilities. Some of the problems formerly cited as disadvantages have been resolved. One that remains is that lack of knowledge of ozonation byproducts.

CHLORINE DIOXIDE

Chlorine dioxide, like ozone, is not widely used as a disinfectant in the United States, although it is effective for that purpose. Because chlorine dioxide is a powerful oxidant, it has been used to control phenolic tastes and odors. It also has been used to control tastes and odors resulting from algal bloom and decaying vegetation in open reservoirs.

Disinfectant comparisons of chlorine dioxide and chlorine at doses less than 1.0 mg/l reveal some of the beneficial characteristics of chlorine dioxide. Chlorine dioxide is slightly less effective as a disinfectant than chlorine at pH 6.5. As pH increases above 7, however, chlorine dioxide maintains its disinfecting capability while hypochlorous acid (HOCl) dissociates to form hypochlorite ion (OCl^{-1}) and chlorate (ClO_3^{-3}), neither of which is an effective disinfectant.

Chlorine dioxide cannot be transported because of its potential explosiveness, so it must be generated at its point of use. Aqueous sodium chlorite (Na_2ClO_2) reacts with aqueous chlorine to form chlorine dioxide. Depending on generator control, untreated chlorine or chlorite may be found in the generator's effluent. Chlorate is also reported to be formed. Chlorine dioxide can also be formed from sodium chlorite, sodium hypochlorite, and sulfuric acid, or from sodium chlorate, sodium chloride, and sulfuric acid. These methods are not commonly employed.

The problems associated with the use of chlorine dioxide are related to its byproducts and end products. The fate of oxidized organic compounds is not completely understood. Work is now underway to define the reaction byproducts that occur when humic acids, synthetic organic chemicals, or natural waters are treated with chlorine dioxide. It has been reported that chlorine dioxide minimizes the formation of chloroform and other THM's if properly controlled, but it is not known what other possibly toxic or carcinogenic substances are formed as byproducts in reaction with natural waters.

Another problem is caused by formation of chlorite, which reportedly has detrimental health effects related to the blood. Work is under way to better define these health effects and to relate them to chlorite concentrations. Chlorite is reported to be an end product of the reaction between chlorine dioxide and natural waters.

Cost of Water Disinfection

Cost of water disinfection was estimated by Symons and colleagues in *Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes* (8). Table 5 was taken from that publication. Disinfection costs may vary by a factor of 10 or more, depending on plant size, disinfectant used, and dose required to attain the desired residual. In general, chlorination is cheaper than using ozone or chlorine dioxide.

Summary

The goal of disinfection has been and still is to produce water that is safe to drink. In the past, this goal was attained by killing pathogens in the water. This remains the purpose of disinfection. In addition, the production of potentially hazardous chemicals during disinfection makes it necessary that all aspects of the local situation be carefully considered before adopting or changing disinfection processes.

TABLE 5. Estimated Cost of Disinfection

Item	Costs,[a] cents per 1,000 gal		
	1-mgd design capacity	10-mgd design capacity	100-mgd design capacity
Chlorination 2 mg/l, 30-minute contact time:			
Chlorine at 10 cents per pound	1.8	0.6	0.4
Chlorine at 20 cents per pound	1.9	0.8	0.5
Ozone 1 mg/l, 20-minute contact time:			
Ozone generated by air	4	1.2	0.7
Ozone generated by oxygen	5	1.3	0.7
Chlorine dioxide 1 mg/l, 30-minute contact time:			
Chlorine at 10 cents per pound	3	1.5	1.2
Chlorine at 20 cents per pound	3	1.5	1.2

[a]These costs will vary at different locations, so should be considered approximate.
Note.–Sodium chlorite cost = 70 cents per pound.

References

1. National Interim Primary Drinking Water Regulations, *Fed. Reg.*, Dec. 24, 1975.
2. Rook, J. J. Formation of Haloforms During Chlorination of Natural Waters. *Water Treat. Exam.*, *23*(2):234, 1974.
3. Bellar, T. A., J. J. Lichtenberg, and R. C. Kroner. The Occurrence of Organohalides in Chlorinated Drinking Water. *J. Am. Water Works Assoc.*, 66:703, 1974.
4. Symons, J. M., T. A. Bellar, J. K. Carswell, J. DeMarco, K. L. Kropp, G. G. Robeck, D. R. Deeger, D. J. Slocum, B. L. Smith, and A. A. Stevens. National Organics Reconnaissance Survey for Halogenated Organics in Drinking Water. *J. Am. Water Works Assoc.*, *67*(11): 634-647, 1975.
5. Love, O. T., Jr., J. K. Carswell, A. A. Stevens, T. J. Sorg, G. S. Logsdon, and J. M. Symons. *Preliminary Assessment of Suspected Carcinogens in Drinking Water—Interim Report to Congress.* App. VI. U.S. Environmental Protection Agency, Washington, D.C., June 1975.
6. Love, O. T., Jr., J. K. Carswell, A. A. Stevens, and J. M. Symons. Treatment of Drinking Water for Prevention and Removal of Halogenated Organic Compounds (An EPA Progress Report). Presented at the 95th Annual Conference of the American Water Works Association, Minneapolis, Minn., June 8-12, 1975.
7. Love, O. T., Jr., J. K. Carswell, A. A. Stevens, and J. M. Symons. Pilot Plant Studies and Measurement of Organics. Presented at 1975 Water Quality Technology Conference, American Water Works Association, Atlanta, Ga., Dec. 8-10, 1975.
8. Symons, J. M. *Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes.* U.S. Environmental Protection Agency, Municipal Environmental Research Laboratory, Water Supply Research Division, Cincinnati, Ohio, 1976.
9. Laubusch, E. J. Chlorination and Other Disinfection Processes. In: *Water Quality and Treatment.* 3rd ed. McGraw-Hill, New York, N.Y., 1971. Ch. 5.
10. White, G. C. *Handbook of Chlorination,* Van Nostrand Reinhold, 1972.
11. Fair, G. M., J. C. Geyer, and D. A. Okun. *Water and Wastewater Engineering.* Vol. 2. John Wiley, New York, N.Y., 1968.
12. Riehl, M. L. *Water Supply and Treatment.* 9th ed. Bulletin No. 211, National Lime Association, Washington, D.C., 1962.
13. Cox, C. R. *Operation and Control of Water Treatment Processes,* World Health Organization Monograph Series No. 49, 1964.

Treatment Techniques for the Removal of Organic Contaminants from Drinking Water

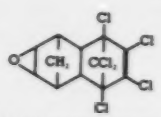
by O. THOMAS LOVE, JR.
Water Supply Research Division, MERL
U.S. Environmental Protection Agency
Cincinnati, Ohio

The National Interim Primary Drinking Water Regulations established maximum contaminant levels (MCL's) for six organic chemicals: endrin, lindane, methoxychlor, and Toxaphene—which are chlorinated hydrocarbons—and two chlorophenoxys, 2,4-D and 2,4,5-TP (Silvex). These six specific organic contaminants can be grouped under the general term "pesticides" and this section summarizes pertinent results from investigators who have examined pesticide removal (i.e., reduction in concentration) by various water treatment techniques.

Occurrence of Pesticides in Water Supplies

Because of the vast and diversified use of these six pesticides in the United States, there is certainly a potential or opportunity for contaminating water supplies with these materials. These organic pesticides are not naturally occurring. They may, for example, enter a drinking water from direct application for control of nuisance vegetation, fish, and aquatic insects; from nonpoint sources such as runoff from agricultural, urban, and suburban areas; from accidental spills; or, of course, from direct wastewater discharge from a point source. A bibliography on the occurrence and fate of pesticides in soils, aquifers, impoundments, lakes, and water courses appears at the end of this section, and pesticide removal by natural processes will not be discussed further. Because pesticide contamination is likely to be intermittent, it presents a potentially troublesome problem to the water plant operator. Distribution system contamination from pesticides is the result either of an inadvertent cross-connection or of sabotage, and control of these situations is not discussed in this section.

Endrin



1,2,3,4,10,10-Hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octanydro-1,4-endo, endo-5,8-dimethane-naphthalene

MCL: 0.0002 mg/l
Molecular Weight: 381
Threshold Odor Concentration: 0.009-0.018 mg/l (1,2)
Odor Type: Musty and chlorinous (2)
Other Names (3,4): Mendrin, experimental insecticide 269, nendrin

Endrin, a chlorinated hydrocarbon, is a potent organic insecticide introduced in the United States in 1951. It received a U.S. patent in 1959. Currently there are several registered uses of endrin. This pesticide is used primarily on field crops because it is nonsystemic and persistent.

Lauer et al. (5) investigated a situation where endrin, applied in sugar cane farming, contaminated a drinking water source. The incident showed that conventional treatment (coagulation, sedimentation, and sand filtration) was ineffective in reducing the contaminant. Similar reports containing field data on treatment plant removal of endrin are scarce because contamination is random and monitoring is not continuous. In the community water supply study (6), performed in 1969, 80 of the 160 samples collected nationwide for pesticide analysis showed

detectable but nonquantifiable traces of endrin. These samples, however, were all collected on finished water and the treatment processes could not be evaluated for pesticide removal.

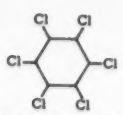
Most of the information on reducing various concentrations of endrin has been gathered through laboratory studies and pilot-scale water treatment plant experiments. The foremost work on this topic was conducted in the early and mid-1960's by Robeck, Dostal, Cohen, and Kreissl (1). This work will be referred to frequently throughout this organics section because two of the six pesticides studied in detail (endrin and lindane) now have established MCL's. Table 6 summarizes the expected removals of endrin by chlorine oxidation, conventional treatment, and conventional treatment supplemented with powdered activated carbon (PAC) or granular activated carbon (GAC).

TABLE 6. Endrin[a] Removal at 0.010-mg/l Load (1)

Unit process	Endrin removal, percent
Chlorination, 5 mg/l	<10
Coagulation and filtration	35
Powdered activated carbon:	
5 mg/l	85
10 mg/l	92
20 mg/l	94
Granular activated carbon, 0.5 gal/min/ft^3	>99

[a]MCL = 0.0002 mg/l.

Lindane



gamma (γ) isomer of 1,2,3,4,5,6–hexachlorocyclohexane

MCL: 0.004 mg/l
Molecular Weight: 291
Threshold Odor Concentration: 0.33-12 mg/l (1,2,7)
Odor Type: Chlorinous medicinal (2)
Other Names (3,4): Gammaexane, Gammopaz, Gexane, Kwell, Lindex, Lindust, Lintox, among many others

Lindane, a chlorinated hydrocarbon, is the most toxic isomer of benzene hexachloride. It was discovered in 1942 and is widely used as an insecticide to control cotton insects and grasshoppers. Nicholson et al. (8,9) conducted a study on a watershed in the southeastern United States, where lindane and other pesticides were used on cotton fields. Varying concentrations of lindane were detected throughout the study in both the river and the effluent from a water treatment plant using the river as a source of drinking water. The water treatment processes consisting of coagulation, sedimentation, filtration, and chlorination were ineffective in reducing the insecticide levels.

With field data lacking, removal of lindane has been the target for several laboratory and pilot plant experiments. Buescher et al. (10) took distilled, deionized, and carbon-filtered water, spiked it with several mg/l lindane and subjected it to chlorine (40 mg/l), hydrogen peroxide (40 mg/l), sodium peroxide (40 mg/l), potassium permanganate (40 mg/l), ozone, and aeration. It is highly unlikely (barring a lindane spill) that the concentration of this pesticide would ever be found in the milligram-per-liter range in a drinking water source; however, it is of interest that only ozone (in concentrations far in excess of disinfection doses) had any appreciable effect on reducing the lindane concentration. Robeck et al. (1), on the other hand, used much lower pesticide concentrations (10-20 μg/l), yet conventional treatment was ineffective, and 5 mg/l chlorine and up to 40 mg/l potassium permanganate did not oxidize or destroy this insecticide. Ozone, however, reduced 20 μg/l lindane by 55 percent when applied at 38 mg/l in a 14-minute contact chamber. Ozone doses over a few mg/l are uncommon in water treatment and Moergeli (11) reported that ozonation sufficient for disinfecting water from Lake Constance, Switzerland, had no effect on lindane concentrations of 40-110 μg/l.

Robeck et al. (1) included both PAC and GAC in their pilot plant studies; the effects when adsorption supplemented conventional treatment are shown in table 7. Hansen (12), reported in 1976 that trace amounts of lindane were reduced below the detectable limit (0.003 μg/l) after passage through GAC beds that had been in service for 14 months.

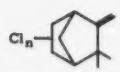
The process of reverse osmosis for lindane removal has been examined by several investigators. Using a cellulose acetate membrane, Smola (12) reported low rejection efficiencies at 30-50-psi pressure for lindane concentrations ranging from 0.007 to 1.93 mg/l. Hindin et al. (14), using a laboratory-scale reverse osmosis cell with a cellulose acetate membrane, reported a 73.4-percent rejection in lindane where the initial concentration was 0.5 μg/l, and an 84-percent reduction when the concentration was 0.05 μg/l. The

pressure differential, however, applied to the feed solution was 100 atmospheres (1,470 psi). Unless the untreated water is very low in turbidity some pretreatment for particulate removal is necessary before reverse osmosis can be effective.

TABLE 7. Lindane[a] Removal by Activated Carbon (3)

Unit process	Lindane removal, percent
Powdered activated carbon:	
5 mg/l	30
10 mg/l	55
20 mg/l	80
Granular activated carbon, 0.5 gal/min/ft^3	>99

[a]Initial lindane level = 0.010 mg/l. MCL = 0.004 mg/l.



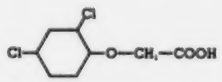
Toxaphene

chlorinated camphene, 67-69 per cent chlorine. Where average n = 8

MCL: 0.005 mg/l
Molecular Weight: 412
Threshold Odor Concentration: 0.005-0.14 mg/l (2)
Odor Type: Musty to moldy (2)
Other Names (3,4): Alltox, Estonox, Chem-phene, Geni-phene, Gy-phene, Phenacide, Phenatox, Toxadust

Toxaphene, a chlorinated hydrocarbon, was introduced in the United States in 1948, patented in 1951, and registered uses are common. A major use is in cotton farming to combat such insects as boll weevils, bollworms, aphid, and leafworm. Contamination of a public drinking water supply by agricultural runoff was reported by Nicholson et al. (9), who found that conventional water treatment practice (coagulation, settling, filtration, and chlorination) was ineffective in reducing Toxaphene concentrations that were variable, but never found to exceed 0.41 μg/l.

Cohen et al. (15,16) experienced similar discouraging removal results in the early 1960's in laboratory studies using much larger concentrations of this insecticide and dosing up to 100 mg/l alum for coagulation. Moreover, neither chlorine nor chlorine dioxide had any effect on removing Toxaphene. Adsorption with activated carbon was more encouraging. An initial concentration of 0.1 mg/l Toxaphene was reduced to 0.007 mg/l by 5 mg/l PAC, so the authors concluded that "no common treatment other than that with activated carbon will remove Toxaphene."



2,4-D

2,4-dichlorophenoxyacetic acid

MCL: 0.1 mg/l
Molecular Weight: 221
Threshold Odor Concentration: 3.13 mg/l (2)
Odor Type: Chlorophenol to musty (2)

2,4-D is a systemic herbicide discovered in 1944. It was patented in the United States in 1949. Registered products are in use (3,4). 2,4-D was one of the first organic compounds used for weed control, and it remains popular for that use.

Aly and Faust (17) made an excellent contribution to the literature by evaluating the common water treatment processes of coagulation, oxidation, and adsorption for the removal of 2,4-D derivatives. Five materials (the sodium salt of 2,4-D, 2,4-Dichlorophenol, and isopropyl, butyl, and isooctyl esters) were selected. It was found that at a 1.0-mg/l load none of these compounds was significantly removed by either aluminum or ferric sulfate (100 mg/l dose) in laboratory coagulation and settling studies. Further, chlorination up to 100 mg/l and the addition of potassium permanganate up to 10 mg/l were ineffective in 2,4-D removal. Powdered activated carbon was effective, and doses required to reduce various levels of the 2,4-D derivatives to MCL are shown in table 8.

Whitehouse (18) conducted laboratory studies to determine the effect of pH and types of PAC in removing 2,4-D from solution; however, the concentrations of adsorbants and adsorbates (100 mg/l level) are thought to be too atypical in water treatment to warrant further details on the results.

Reverse osmosis needs additional study before it can be suggested as an effective technique for removing 2,4-D from drinking water. Lonsdale et al. (19) reported a 92.8-percent rejection of 2,4-D from a 1-percent NaCl solution having an initial herbicide concentration of 35 mg/l. Edwards and Schubert (20) found that 2,4-D rejections from a 50-mg/l solution never exceeded 65 percent initially, and near the end of each run rejection efficiencies ranged from 1 to 51 percent. These studies used small

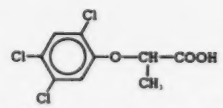
reverse osmosis cells at pressures ranging from 80 to 1,500 psi. In addition to pretreatment considerations with reverse osmosis, the reject water constitutes a separate disposal problem that must be included in the overall evaluation and cost estimation of the method.

TABLE 8. Carbon Doses Required to Reduce the Concentration of 2,4-D Compounds to Maximum Contaminant Limit[a] (MCL) (17)

Initial concentration,[b] mg/l	Powdered activated carbon dose, mg/l			
	Sodium salt	Isopropyl ester	Butyl ester	Isooctyl ester
10	306	150	165	179
5	153	74	82	89
3	92	44	49	53
1	31	14	15	16

[a] MCL = 0.1 mg/l.
[b] Expressed as the acid equivalent.

2,4,5-TP (Silvex)



2,4,5-trichlorophenoxypropionic acid

MCL: 0.01 mg/l
Molecular Weight: 269
Threshold Odor Concentration: 0.78 mg/l (2)
Odor Type: Idodform (2)
Other Names (3,4): Kuron, Kurosol, Aqua Vex, O-X-D

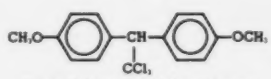
Silvex is a postemergent herbicide used for controlling brush, aquatic vegetation, woody plants, and certain weeds not susceptible to 2,4-D. It was introduced in the United States in 1952. Currently there are several registered uses of this herbicide.

Treatment data for the removal of this compound from drinking water are not available in 1977. Robeck et al. (1) examined the butoxy ethanol ester of 2,4,5-T; if it is assumed (until more definitive information becomes available) that the two compounds would behave similarly in a dilute aqueous solution, table 9 may be useful as a summary of expected removals.

TABLE 9. 2,4,5-T Ester Removal at 0.01-mg/l Load (3)

Unit process	2,4,5-T ester removed, percent
Chlorination, 5 mg/l	<10
Coagulation and filtration	65
Powdered activated carbon:	
5 mg/l	80
10 mg/l	80
20 mg/l	95
Granular activated carbon	>99

Methoxychlor



1,1,1-trichloro-2,2-bis(p-methoxyphenyl)ethane

MCL: 0.1 mg/l
Molecular Weight: 346
Threshold Odor Concentration: 4.7 mg/l (2)
Odor Type: Musty to chlorinous (2)
Other Names (3,4): DMDT, dimethoxy-DT, dianisyl trichloroethane, Marlate

Methoxychlor is a chlorinated insecticide used to control external parasites on animals. Treatment information is not available on this insecticide in 1977. It is very likely, however, that adsorption with GAC would remove this contaminant effectively from drinking water.

Summary of Treatment Techniques

The organic compounds for which MCL's have been established are the pesticides endrin, lindane, Toxaphene, 2,4-D, 2,4,5-TP, and methoxychlor. There is a varying amount of information on the removal of the first four materials from drinking water, but the author was unable to locate pertinent studies referenced on the removal of 2,4,5-TP and methoxychlor. Data gaps in table 10 emphasize the need for additional research on a number of aspects of the removal of organics from drinking water.

In spite of limited specific information, it is apparent that adsorption is more effective than

TABLE 10. Percent Organics Removed by Water Treatment Processes, Summary

Process	Endrine[a] reduction (3,23)		Lindane[b] reduction (3,23)		Toxaphene[c] reduction (15,16)		2,4-D[d] reduction (17)							
							Sodium salt		Isopropyl ester		Butyl ester		Isooctyl ester	
	Reported	Needed[e]	Reported	Needed[e]	Reported	Needed[e]	Reported	Needed[e]	Reported	Needed[e]	Reported	Needed[e]	Reported	Needed[e]
Coagulation, filtration	35	98	<10	60	<10	([f])	<10	90	<10	90	<10	90	<10	90
Coagulation, filtration, and adsorption with:														
Powdered activated carbon, mg/l:														
5-9	85	98	30	60	93	95								
10-19	92	98												
	80	90	55	60										
20-29	94	98	80-90	60					90	90	90	90	90	90
30-39							90	90						
40-49														
50-59	98	98							97	97	97	97		
70-79			99	60									97	97
Granular activated carbon, 7-5-minute full bed contact time	>99	98	>99	60					98	98				
Oxidation:														
Chlorine, mg/l:														
5	<10	98	<10	60										
8			<10	([f])										
50			<10	([f])										
100					<10	98	<10	90	<10	90	<10	90	<10	90
Ozone, mg/l:														
11			<10	60										
38			55	80										
Potassium permanganate, mg/l														
10			<10	60										
40			<10	60			<10	90	<10	90	<10	90	<10	90

[a]MCL = 0.0002 mg/l.
[b]MCL = 0.004 mg/l.
[c]MCL = 0.005 mg/l.
[d]MCL = 0.1 mg/l.
[e]Reduction in test concentrations necessary to meet MCL.
[f]Initial test concentration was less than MCL.
NOTE.—Treatment information not available for methoxychlor (MCL = 0.1 mg/l) and 2,4,5-TP (MCL = 0.1 mg/l).

TABLE 11. Activated Carbon, mg/l, Required to Reduce the Pesticide Level in Distilled Water and in Little Miami River Water (23)

Pesticide	Method	10-μg/l initial level		1.0-μg/l initial level	
		1.0 μg/l after treatment	0.1 μg/l after treatment	0.1 μg/l after treatment	0.05 μg/l after treatment
2,4,5-T ester	Jar test[a]	2.5	17	1.5	3
	Plant treatment[b]	14	44	3	5
Endrin	Jar test[a]	1.8	14	1.3	2.5
	Plant treatment[b]	11	126	11	23
Lindane	Jar test[a]	2	12	1.1	2
	Plant treatment[b]	29	70	6	9

[a]Pesticide is removed from distilled water by activated carbon alone, with a contact time of an hour.
[b]Pesticide is removed from river water by conventional treatment and activated carbon.

conventional treatment or oxidation for pesticide removal. The effectiveness of adsorption is influenced by the temperature and pH of the water, but to a greater degree adsorption depends on:

- Concentrations of adsorbant and adsorbate
- Contact or residence time
- Competition for available adsorption sites

Competitive adsorption is important to recognize because it dramatically affects the amount of adsorbant available for the contaminant. Table 11 illustrates this point. In one instance the pesticides are removed from distilled water by PAC alone, and in the other, a similar pesticide concentration is removed from river water by conventional treatment supplemented with PAC. Where pesticide was added to the river water (i.e., where competition for the adsorption sites existed), the PAC doses were 4 to 14 times higher than the companion noncompetitive situation. Studies are underway to further examine competitive adsorption (21,22). Until the phenomenon is better understood, it is impossible to predict with much certainty a PAC dose effective for variations in water quality.

Robeck (23) commented that, because pesticides and their carrier solvents have odors, water plant operators treating for odor removal will provide some incidental protection by reducing certain pesticides. When the comment was made, in 1972, the MCL's in the EPA Guidelines for Pesticides in Water (24) were quite similar to the threshold odor concentrations (TOC's). In 1977, however, the MCL is more rigid and differs from the odor detection level for some pesticides by several orders of magnitude (see table 12). Note that the TOC's given for these pesticides were acquired under laboratory conditions using "pure" compounds and odor-free water. The odor of these pesticides (table 12) or of their reaction products after chlorination is not known, however, and could vary significantly (1,16,25). Relying on odors to signal pesticide contamination, or relying on intermittent odor control by PAC to insure a safe pesticide level is risky and considered poor practice.

TABLE 12. Threshold Odor Concentration (TOC) and Maximum Contaminant Level (MCL) of Pesticides in Water

Pesticide	TOC (3,4,17,15), mg/l	MCL, mg/l
Endrin	0.009-0.018	0.0002
Lindane	0.33-12	0.004
Toxaphene	0.005-0.14	0.005
Methoxychlor	4.7	0.1
2,4-D	3.13	0.1
2,4,5-TP	0.78	0.01

A few milligrams per liter of PAC may be adequate for odor control, but, according to available pesticide treatment information, several milligrams per liter are required to effect organic removals, and the sludge created is sometimes troublesome and difficult to manage. A plant operator using PAC should consider multiple points of injection for maximum efficiency

of the adsorbant and possibly for better removals (1,26).

Because of the uncertainties involved in pesticide occurrence, GAC beds that are continuously on line offer the best barrier against pesticide contamination (23,26). Organic pesticides have been demonstrated to be very strongly adsorbed both on virgin GAC and on GAC considered exhausted for odor control (1). The life of a GAC bed for pesticide removal is not indefinite, but it has been suggested that replacing or reactivating a GAC bed because of odor penetration is an adequate guideline for controlling pesticides (23). Granular activated carbon can be used directly (no pretreatment) with low-turbidity ground waters or as a filter/adsorber in a conventional or direct filtration plant.

Estimating Cost for Reducing Trace Organics (Pesticides) Below MCL

ADSORPTION WITH PAC

The following assumptions are made in estimating the cost of adding PAC for controlling pesticides in drinking water:

- A filtration plant already exists.
- PAC is already being fed for odor control.
- Sludge-handling facilities and disposal are adequate for the additional imposed loadings.
- Analytical costs for pesticide analysis are excluded.
- PAC costs 30 cents per pound.
- A PAC dose of 5-80 mg/l would allow for a contamination level from 2.5 to 50 times the MCL.

On these assumptions the estimated cost would be 1.2-20 cents per 1,000 gallons.

ADSORPTION WITH GAC

One of the most rigorous and complete documents for estimating GAC costs was developed by Clark and coworkers (27). Although not addressed to pesticide removal, most of the parameters and indices used are applicable to any fixed-bed adsorption process. If it is assumed that penetration of odor compounds precedes pesticide breakthrough, costs for odor removal by GAC should be an estimated cost for pesticide removal. For example, an existing 1-mgd filtration plant operating at 70-percent capacity replaces 30 inches of sand with GAC, which effectively removes odors for 12 months. The adsorption (pesticide removal) process would cost an estimated 3.3 cents per 1,000 gallons. It is assumed that:

- GAC costs 38 cents per pound and the amount needed varies directly with the plant size.
- Interest and labor costs are negligible.
- Attrition loss is small and GAC is replaced when exhausted (no on-site reactivation).

Table 13 then summarizes the expenditures that might be expected for pesticide removal by GAC for time periods appropriate for the expected life of GAC for odor removal. Hansen (1,28) has studied very closely the actual costs for GAC adsorption at his water utility in Mount Clements, Michigan. His costs, shown in table 13, are lower than the estimate because of differences in the unit costs and amounts of GAC used in each situation.

TABLE 13. Costs of Granular Activated Carbon (GAC) Adsorption for Pesticide Removal

Costs, cents per 1,000 gal	GAC replacement frequency, months			
	12	24	36	48
Estimated	3.3	1.6	1.1	0.8
Actual (3,28)	—	—	0.5	0.4

References

1. Robeck, Gordon G., Kenneth Dostal, Jesse Cohen, and James Kreissl. Effectiveness of Water Treatment Processes in Pesticide Removal. *J. Am. Water Works Assoc.*, 57:181-199, 1965.
2. Sigworth, E. A. Identification and Removal of Pesticides and Herbicides. *J. Am. Water Works Assoc.*, 57:1016-1022, 1965.
3. *Cleaning Our Environment—The Chemical Basis for Action.* Report, American Chemical Society, Committee on Chemistry and Public Affairs, Subcommittee on Environmental Improvement, Washington, D.C., 1969. Pp. 193-197.

4. Packer, K., ed. Nanogen Index—A Dictionary of Pesticides and Chemical Pollutants. Nanogen International, Freedom, Calif., 1975. Pp. 36-90.
5. Lauer, E. J., H. P. Nicholson, W. S. Cox, and J. I. Teasley. Pesticide Contamination of Surface Waters by Sugar Cane Farming in Louisiana. *Trans. Am. Fish. Soc., 95*:310, 1966.
6. McCabe, L. J., J. M. Symons, R. D. Lee, and G. G. Robeck. Survey of Community Water Supply Systems, *J. Am. Water Works Assoc., 62*:670, 1970.
7. Faust, S. D., and O. M. Aly. Water Pollution by Organic Pesticides, *J. Am. Water Works Assoc., 56*:267-274, 1965.
8. Nicholson, H. P. Pesticide Pollution Studies in the Southeastern U.S. Robert A. Taft Engineering Center, Cincinnati, Ohio, 1962.
9. Nicholson, H. P., A. R. Grzenda, and J. I. Teasley. Water Pollution by Insecticides, A Six and One-half Year Study of a Water Shed. In: *Proceedings of the Symposium on Agricultural Waste Water*, U.S. Environmental Protection Agency, Atlanta, Ga., 1966. P 132.
10. Buescher, C. A., J. H. Dougherty, and R. T. Skrinde. Chemical Oxidation of Selected Organic Pesticides. *J. Water Pollut. Control Fed., 36*: 1005-1112, 1964.
11. Moergeli, B. Removal of Pesticides from Drinking Water, *Sulzer Tech. Rev., 54*(2):91-6, 1972.
12. Hansen, R. E., Organics Removal of Mount Clemens, Michigan. Presented to Michigan Section of the American Water Works Association, Ann Arbor, Mich., Jan. 1977.
13. Smola, D. J. Removal of Toxic Pesticides by Reverse Osmosis Water Treatment. Master's thesis, Massachusetts University, Amherst Department of Civil Engineering, Dec. 1968. P. 104.
14. Hindin, E., Baul J. Bennett, and S. S. Narayanan. Organic Compounds Removed by Reverse Osmosis. *Water Sewage Works, 116*:466-471, 1969.
15. Cohen, J. M., L. J. Kamphake, A. E. Lemke, C. Henderson, and R. L. Woodward. Effects of Fish Poison on Water Supplies. Part 1. Removal of Toxic Materials. *J. Am. Water Works Assoc., 52*:1551-1566, 1960.
16. Cohen, J. M., G. A. Rourke, and R. L. Woodward. Effect of Fish Poisons on Water Supplies. Part 2. Odor Problems. *J. Am. Water Works Assoc., 53*:49-57, 1961.
17. Aly, O. M., and S. D. Faust. Removal of 2,4-D Derivatives from Natural Waters. *J. Am. Water Works Assoc., 57*:221-230, 1965.
18. Whitehouse, J. D. A Study of the Removal of Pesticides from Water. University of Kentucky, Water Resources Institute, Research Report No. 8, Lexington, Ky. 1967.
19. Lonsdale, H. K., C. E. Milstead, B. P. Cross, and F. M. Graber. Study of Rejection of Various Solutes by Reverse Osmosis Membranes. R and D Report No. 447. Office of Saline Water, Washington, D.C., July 1969. 72 pp.
20. Edwards, V. H., and Paul F. Schubert. Removal of 2,4-D and Other Persistent Organic Molecules from Water Supplies by Reverse Osmosis. *J. Am. Water Works Assoc., 66*:610-616, 1974.
21. EPA Grant No. R8034730. Activated Carbon Adsorption of Trace Organic Compounds. Research in progress. Principal investigator: V. Snoeyink, University of Illinois. Project officer: A. Stevens, MERL, WSRD, Cincinnati, Ohio 45268. Completion date: summer 1977.
22. EPA Grant No. R804639. Effectiveness of Activated Carbon for Removal of Toxic and/or Carcinogenic Components from Water Supplies. Research in progress. Principal investigator: W. Weber, University of Michigan. Project Officer: A. Stevens, MERL, WSRD, Cincinnati, Ohio 45268. Completion date: 1979.
23. Robeck, Gordon G. Purification of Drinking Water to Remove Pesticides and Other Poisonous Chemicals: The American Practice. In: *Proceedings of the 9th Congress of the International Water Supply Association*, London, U.K., September 11-14, 1972.
24. Unpublished working manuscript, U.S. Environmental Protection Agency, Water Supply Programs, Washington, D.C., Oct. 1971.
25. Woodward, R. L. Significance of Pesticides in Water Supplies. *J. Am. Water Works Assoc., 52*:1367-1372, 1960.
26. Love, O. T., Jr., J. K. Carswell, A. A. Stevens, and J. M. Symons. Evaluation of Activated Carbon as a Drinking Water Treatment Unit Process. Mimeo, U.S. Environmental Protection Agency, Cincinnati, Ohio, Mar. 3, 1975. 17 pp.
27. Clark, R. M., D. L. Guttman, J. L. Crawford, and J. A. Machifko. The Cost of Removing Chloroform and Other Trihalomethanes From Drinking Water Supplies. In: James M. Symons, *Interim Treatment Guide for the Control of Chloroform and Other Trihalomethanes*. U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1976. App. 1.

28. Hansen, Robert E. Problems Solved During 92 Months of Operation of Activated Granular Carbon Filters. In: *Proceedings of the 3rd Annual AWWA Water Quality Technology Conference*. Atlanta, Ga., Dec. 1975.

Bibliography—Occurrence and Fate of Pesticides in the Environment

Aly, O. M., and S. D. Faust. Studies on the Fate of 2,4-D and Ester Derivatives in Natural Surface Waters. *J. Agric. Food Chem., 12*:541-544, 1964.

Boucher, Francis R., and G. Fred Lee. Adsorption of Lindane and Dieldrin Pesticides on Unconsolidated Aquifer Sands. *Environ. Sci. Technol., 6*.6;538-543.

Brown, E., and Y. A. Nishioka. Pesticides in Western Streams, A Contribution to the National Programs. *Pest. Monit. J., 1*:38, 1967.

Crosby, D. G., and H. O. Tutass. Photodecomposition of 2,4-D, *J. Agric. Food Chem., 14*:596-599, 1966.

DeMarco, J., J. M. Symons, and G. G. Robeck. Synthetic Organics in Stratified Impoundments, *J. Am. Water Works Assoc., 59*, 1967.

Edwards, C. A. *Persistent Pesticides in the Environment.* Chemical Rubber Company, Cleveland, Ohio, 112-113, 1973.

Huang, Ju-chang. Effect of Selected Factors on Pesticide Sorption and Desorption in the Aquatic System. *J. Water Pollut. Control Fed., 43*(8): 1739-1748, 1971.

Huang, Ju-Chang, and Cheng-Sun Liao. Adsorption of Pesticides by Clay Minerals. *ASCE Sanit. Eng. Div., SA5*:1003-1077, 1970.

King, Paul H., H. H. Yeh, Pierre S. Warren, and Clifford Rancall. Distribution of Pesticides in Surface Waters, *J. Am. Water Works Assoc., 61*:483-486, 1969.

Leigh, G. M. Degradation of Selected Chlorination Hydrocarbon Insecticides. *J. Water Pollut. Control Fed., 41*(11):R450, 1969.

Rosen, A. A., and F. M. Middleton, Chlorinated Insecticides in Surface Waters. *Anal. Chem., 31*:1729-1733, 1959.

Weaver, L. G., G. G. Gunnerson, A. W. Breidenbach, and J. L. Lichtenberg. Chlorinated Hydrocarbon Pesticides in U.S. River Basins. U.S. Public Health Report No. 80, 1965. Pp. 481-493.

Treatment Techniques for the Removal of Radioactive Contaminants from Drinking Water

by GARY S. LOGSDON
Water Supply Research Laboratory, MERL
U.S. Environmental Protection Agency
Cincinnati, Ohio

The National Interim Primary Drinking Water Regulations (1) established maximum contaminant levels (MCL's) for two categories of radioactive contaminants—alpha emitters and beta and photon emitters. The beta and photon emitters are generally manmade radioisotopes rather than naturally occurring ones. Because terms and definitions associated with radioactivity not in everyday use by most water utility people, a glossary is included at the end of this section.

Different types of ionizing radiation may cause different levels of biological damage, even though the amount of energy involved is the same for each type of radiation. For this effect, the term "quality factor" (QF) is used. The QF is a property of the nature and energy of the absorbed radiation. A high QF indicates that the type of radiation in question has a greater potential for causing biological damage, whereas a low QF indicates that the radiation in question would be less biologically damaging if the absorbed energy were equal in both cases. Table 14 gives some of the relationships among the various radiation units.

In general, for beta and gamma radiation the absorbed dose and biological effect or damage are related 1 to 1. Alpha particles, however, are assumed to be 10 times more damaging, as compared to beta and gamma radiation, rad for rad, because one rad of alpha radiation would be absorbed in a very small volume of biological material, so that each cell would be exposed to more ionizing radiation.

TABLE 14. Relationships Among Radiation Units

Type of radiation	Quality factor			
	R	rads	(QF) (2)	rem
X-rays and gamma rays	1	1	1	1
Beta particles	–	1	1[a]	1[a]
Thermal neutrons	–	1	5	5
Fast neutrons	–	1	10	10
Alpha particles	–	1	10	10

[a]In 1966, the International Commission on Radiation Protection (ICRP) recommended that the QF for low energy beta radiation less than 0.03 MeV be assigned a value of 1.7. In 1969 the ICRP amended its earlier recommendation, suggesting the use of 1 as a QF for all beta radiation. The National Council on Radiation Protection and Measurements recommends a QF of 1.

Alpha Emitters

MAXIMUM CONTAMINANT LEVELS

The MCL's for alpha emitters are 5 pCi/l for radium-226 and radium-228, and 15 pCi/l for gross alpha activity including radium-226, but excluding radon and uranium.

RADIUM IN WATER SUPPLIES

Radium is present in water as a naturally occurring element, primarily in ground waters and to a lesser extent in surface waters. Studies by Hursh (3) on the water supply sources of 41 cities in the United States showed the average radium-226 concentration of those municipal water supplies that used surface sources to be less than 0.3 pCi/l, ranging from 0.002 to 3.7 pCi/l. Numerous studies on ground water supplies in areas of radium-bearing deposits have demonstrated radium-226 concentrations ranging from about 0.5 pCi/l to more than 50 pCi/l. The EPA (4) has estimated that as many as 500 public water supplies may exceed the 5-pCi/l radium concentration.

The major radiation problems in ground waters are thought to be caused by leaching of radium from radium-bearing rock strata into the deep sandstone aquifers in Iowa and Illinois, and by leaching of radium from phosphate rock deposits into the Florida aquifer. Elevated radium levels have also been associated with surface run-off water in the vicinity of uranium-rich deposits in Colorado and New Mexico.

REMOVAL OF RADIUM FROM WATER

The water treatment plant is the point of control between radium dissolved or suspended in raw water supplies and the consumer. To meet the interim standard of 5 pCi/l in a cost-effective manner, it is important to understand how the treatment process affects the level of radium in potable water.

The major problem of concern in public water supplies is soluble radium in ground water. Soluble radium exists in water as a divalent ion, similar in chemical behavior to calcium and magnesium. Softening treatment methods have been shown to be effective in removing 70-99 percent of dissolved radium, as have membrane desalting methods. Coagulation without softening may remove up to 25 percent of radium; however, the results are variable and difficult to control.

The three methods selected for analysis in this document are:

- Lime or lime-soda softening (precipitative softening)
- Ion exchange softening
- Reverse osmosis

Radium removal efficiencies and associated operating data from water treatment plants in Illinois (5), Iowa (6), and Florida (7) have been compiled and analyzed herein. Removal efficiencies for each of three treatment methods and associated costs of treatment and waste disposal are reported for each type of plant in the following sections.

Lime or Lime-Soda Softening. Radium removal by lime softening can be related to hardness removal (fig. 47) and pH of treatment (fig. 48). Lime softening can remove 80-90 percent of the radium; therefore, it is suitable for raw waters containing up to 25 pCi/l. To achieve these removals, the process pH would have to be above 10.0.

Ion Exchange Softening. Radium removal by ion exchange is related to hardness removal. Well-operated ion exchange plants can remove 95 percent or more of the radium in raw water (fig. 49). Because radium removal still takes place for a period of time after the resin ceases to remove hardness (Ca^{+2} and Mg^{+2}), regeneration to achieve good hardness removal will assure good radium removal. Naturally, blending of raw and softened water recontaminates the treated water with radium. This practice is common for ordinary municipal zeolite softening plants, but it could result in production of a water exceeding the radium MCL in some instances. Blending must be given careful study before it is used at a radium removal plant.

Reverse Osmosis. Osmosis is the spontaneous passage of liquid from a dilute to a more concentrated solution across an ideal semipermeable membrane that allows passage of the liquid but not of dissolved solids. Reverse osmosis is a process in which the natural osmotic flow is reversed by the application of pressure to the concentrated solution sufficient to overcome the natural osmotic pressure of the less concentrated (dilute) solution. When the amount of water passing in either direction is equal, the applied pressure can be defined as the osmotic pressure of the dilute solution having that particular concentration of solutes.

In practical applications, pumps are used to supply the pressure to overcome osmotic pressure. The water flow rate through the membrane depends primarily on the net driving pressure. The solute flow rate through the membrane depends almost solely on the solute concentration of the feed water.

The pumping pressure required to provide the driving force in the reverse osmosis process is a direct function of the concentration of dissolved solids in the feed. Reverse osmosis applications have been

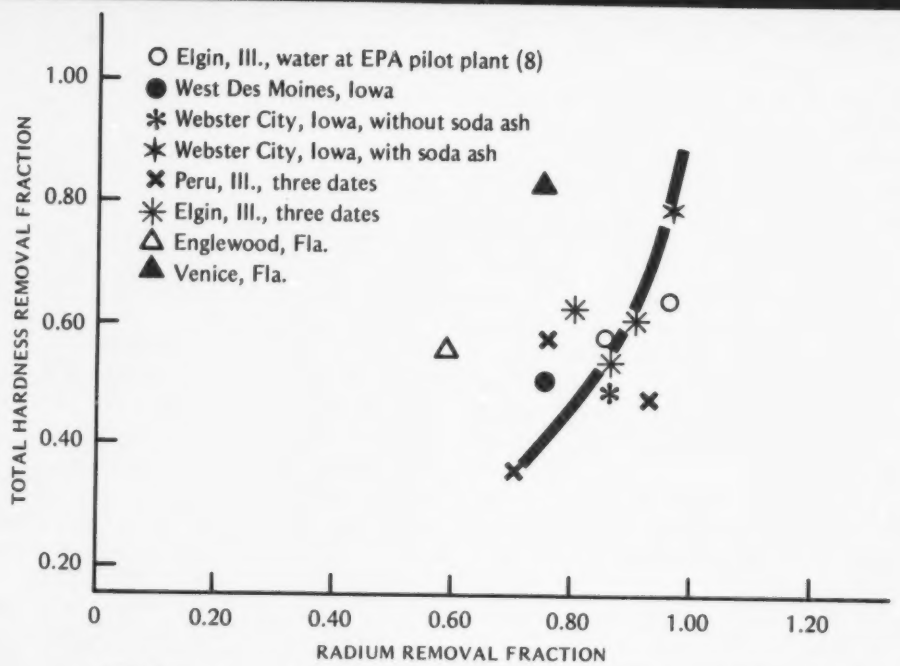


FIGURE 47 LIME-SODA PROCESS, TOTAL HARDNESS REMOVAL FRACTION VERSUS RADIUM REMOVAL FRACTION (7)

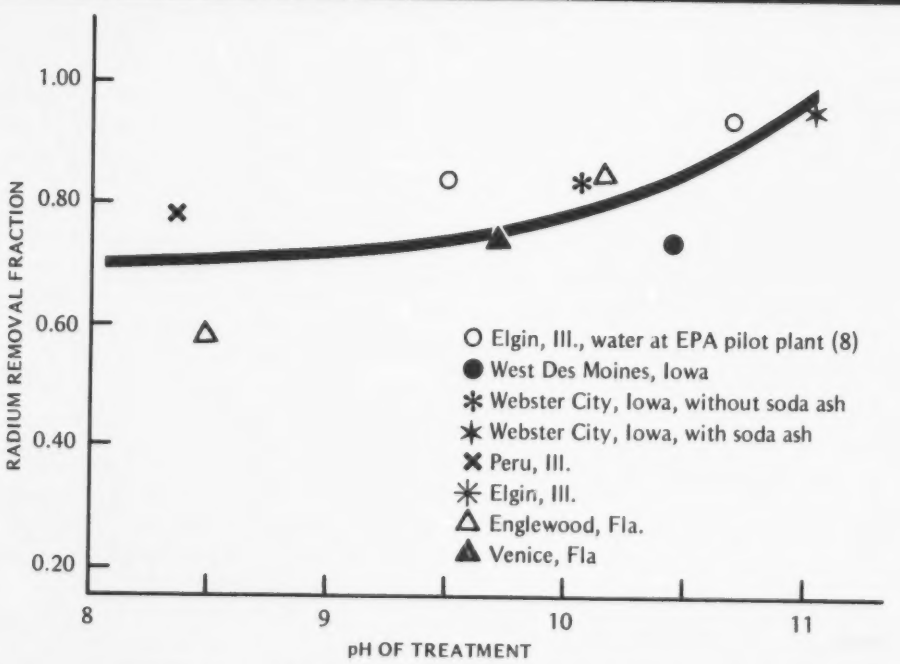


FIGURE 48 RADIUM REMOVAL FRACTION VERSUS pH OF TREATMENT, LIME-SODA PROCESS (7)

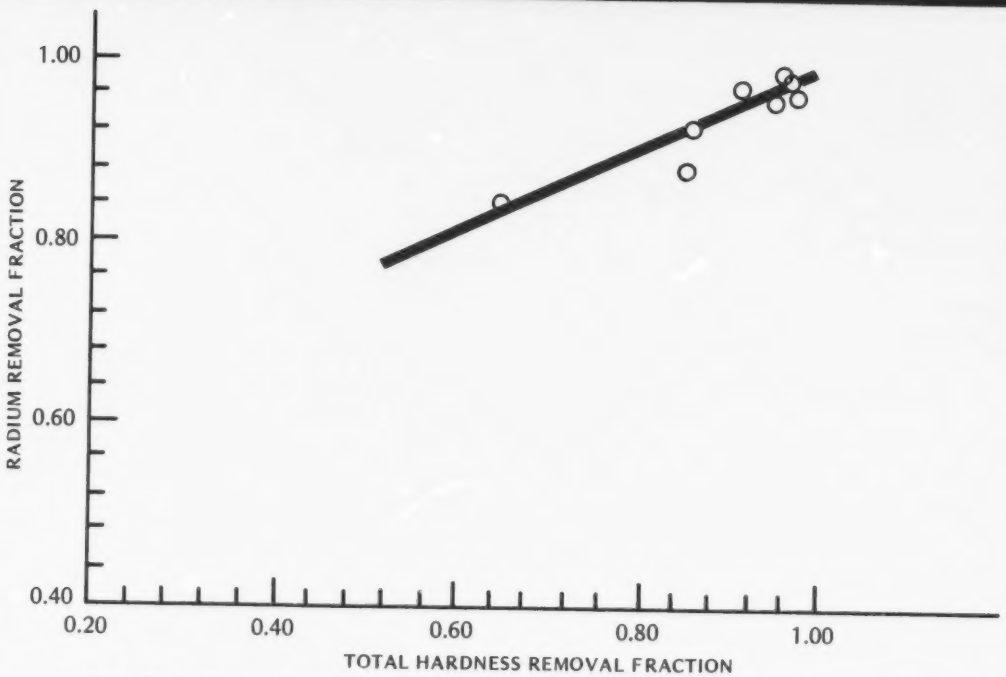


FIGURE 49 RADIUM REMOVAL FRACTION VERSUS TOTAL HARDNESS REMOVAL FRACTION IN ION EXCHANGE PLANTS, BEFORE BLENDING (7)

primarily for feed water with total dissolved solids (TDS) above a minimum of 2,000 mg/l, and usually in the range of 4,000-35,000 (sea water) mg/l TDS.

A characteristic of semipermeable membranes used for reverse osmosis is that their rejection is greater of multivalent ions, such as Ca^{+2}, Mg^{+2}, Ra^{+2}, and SO_4^{-2}, than of monovalent ions Na^{+1}, Cl^{-1}, and so forth. The primary advantages of reverse osmosis are its high rate of rejection of dissolved solids in the raw water and its suitability for use in small systems. There are some disadvantages to reverse osmosis, including:

- High initial and operating costs
- Need for pretreatment of raw water with turbidity removal; treatment with acid and other chemicals to prevent fouling of the membranes by slimes, suspended solids, iron, and manganese; and precipitation of calcium carbonate and magnesium hydroxide
- Need to stabilize finished water with lime or other chemicals to prevent corrosion in distribution system

Table 15 presents radium removal data from two reverse osmosis plants. The Greenfield plant removed 93 percent of the TDS and 96 percent of the radium-226. The difference between TDS removal and radium removal results from the amount of monovalent ions that passed through the membrane.

It will be assumed, for purposes of this report, that a well-operated reverse osmosis unit can remove 95 percent of the influent radium activity.

DISPOSAL OF TREATMENT WASTE

Each of the treatment processes for removing radium from potable water generates a waste stream of some sort. These wastes must be disposed of in an environmentally acceptable manner. This section is based on a more comprehensive report prepared by Singley et al. (7).

Methods for Lime Sludge Disposal. Alternatives for disposal of lime sludges are numerous and varied. There follow several of the more important.

TABLE 15. Radium Removal in Reverse Osmosis Plants

Plant	Radium			TDS		
	In, pCi/l	Out, pCi/l	Percent removal	In, mg/l	Out, mg/l	Percent removal
Greenfield, Iowa	14.0	0.6	96	2,160	164	92
Sarasota Bay MHP, Fla. (9)	22.0	0.8	96	–	–	–

- Discharge
  - To sanitary sewers
  - To local receiving water
  - By wet pumping or trucking to local sanitary landfill
- Storage
  - Permanent lagooning
  - Sanitary landfill
    a. with prior temporary lagooning
    b. with prior mechanical dewatering: vacuum filtration, centrifugation, others
  - Other natural or manmade depressions (all with some dewatering before transportation)
    a. strip mine areas
    b. borrow pits and quarries
    c. others
- Use
  - Direct without drying: farmland and pasturelands
  - With prior dewatering
    a. farmland and pastureland
    b. road stabilization
    c. calcination and recycle
- Disposal
  - Direct, recharge to aquifers
  - With prior dewatering: salt mines, coal mines, and so forth
  - As a nuclear waste

Methods for Lime Softening Backwash Disposal. Alternatives for disposal of filter backwash are fewer than for the lime sludges. Some methods will depend on location, plant capacity, and operational factors. Several of the more important alternatives follow.

- Discharge
  - To sanitary sewer
  - To local receiving water
- Storage
  - Tanks or lagoons
    a. for settling and decanting into receiving water
    b. for settling and pumping supernatant back to plant
- Disposal as a nuclear waste

Ion Exchange Brine Disposal. One of the problems created by sodium cycle ion exchange softening is the disposal of spent brine from the regeneration cycle. In view of the increasing water pollution control requirements, these high salinity waters may face severe limits on discharge. The problem becomes even more sensitive when the waste contains elevated levels of radium.

The waste products from the brine and rinse cycle are composed primarily of the chlorides of calcium and magnesium and the excess salt necessary for regeneration. The total solids in a composite sample may vary from an average concentration of 50,000-100,000 mg/l to a maximum of 70,000-200,000 mg/l.

Disposal techniques may be limited by considerations of salinity rather than radium concentration. A list of potential alternatives for handling the wastewater streams follows:

- Discharge
  - To sanitary sewer
  - To local receiving water
    a. streams
    b. oceans
- Storage
  - Evaporation lagoons
  - Land spreading
- Use-recovery
- Disposal
  - In deep aquifers
  - In oil well fields
  - As nuclear wastes

Disposal of Reverse Osmosis Waste. Dissolved solids rejected by the membrane in a reverse osmosis unit flow from the unit in a more concentrated waste stream in a continuous flow. The Greenfield plant was reported to convert 67 percent of the flow to potable water, wasting 33 percent of the raw water flow as brine (10). Because the waste is produced continuously in large volumes, waste strength (3-4 times the raw water concentration) is lower than ion exchange brine strength. Disposal to a sewer may be feasible for reverse osmosis waste.

TREATMENT AND DISPOSAL COSTS TO REMOVE ALPHA EMITTERS

Costs of water treatment for radium removal were calculated by Singley et al. (7). Their computations were based in part on work by Volkert (11). Singley et al. based cost calculations on the need to treat waters with low, medium, and high TDS concentrations and low, medium, and high radium concentrations (see table 16).

The costs of treatment for radium removal are indicated in figures 50 through 55, based on treating to the radium standard of 5 pCi/l raw waters with radium concentrations of 7.5, 20, and 50 pCi/l, respectively.

Unit costs of treatment for radium removal decrease as plant capacity increases, but increase with higher TDS values and higher raw water radium concentrations. The estimated costs in figures 50-55 do not include waste treatment costs. Reverse osmosis is the most expensive process, although it is the most suitable for automated plant operation and use in small plants. Ion exchange, which is generally used in a batch process, is estimated to be the least costly. Lime softening has most frequently been the process of choice for large treatment plants.

TABLE 16. Raw Water Quality Concentrations Assumed for Calculations of Radium Removal Costs

Item	mg/l as $CaCO_3$	mg/l as ion	pCi/l
High level solids:			
TDS	-	2,000	
TH	750	-	
Ca^{+2}	500	200	
Mg^{+2}	250	60	
Alk	300	360	
HCO_3^{-1}	-	-	
Medium level solids:			
TDS	-	1,000	
TH	300	-	
Ca^{+2}	200	80	
Mg^{+2}	100	24	
Alk	200	244	
HCO_3^{-1}	-	-	
Radium concentrations:			
Low level			7.5
Medium level			20
High level			50

Manmade Radionuclides, or Beta and Photon Emitters

MAXIMUM CONTAMINANT LEVELS

The average annual concentration of beta particle and photon radioactivity from manmade radionuclides in drinking water shall not produce an annual dose equivalent to the total body or any internal organ greater than 4 mrem/yr.

Except for the radionuclides listed in table 17, the concentration of manmade radionuclides causing 4 mrem total body or organ dose equivalents shall be calculated on the basis of a 2-l/d drinking water intake using the 168-hour data listed in *Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure* (12), as amended August 1963. If two or more radionuclides are present, the sum of their annual dose equivalent to the total body or to any organ shall not exceed 4 mrem/yr.

TABLE 17. Average Annual Concentrations Assumed to Produce a Total Body or Organ Dose of 4 mrem/yr

Radionuclide	Critical organ	pCi/l
Tritium	Total body	20,000
Strontium-90	Bone marrow	8

If other beta or gamma emitters are present in the water, the nuclides should be identified and quantified, so that a health physics expert can calculate the estimated dose in milligrams per year resulting from drinking 2 l/d of the water. Article 141.16 of the Interim Drinking Water Regulations states that this shall be done if the gross beta particle activity exceeds 50 pCi/l.

It is not anticipated that the limits for beta and photon radiation will be exceeded. Rather, the standard has been promulgated to prevent the degra-

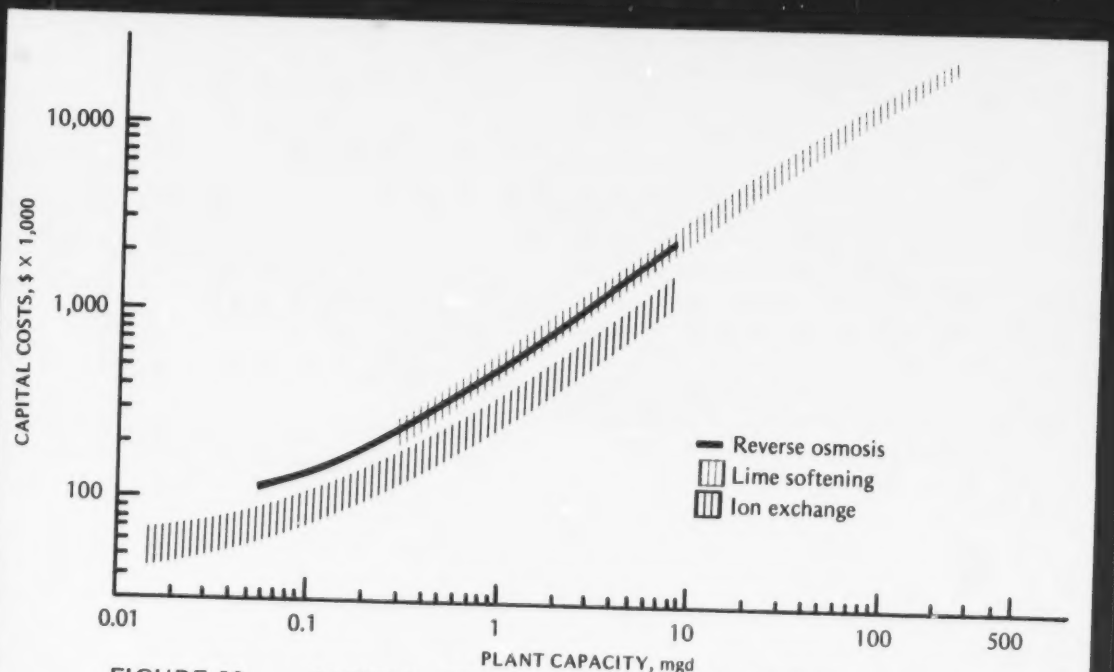


FIGURE 50 CAPITAL COST FOR WATER TREATMENT PLANTS FOR 7.5 pCi/l RADIUM-226 IN RAW WATER

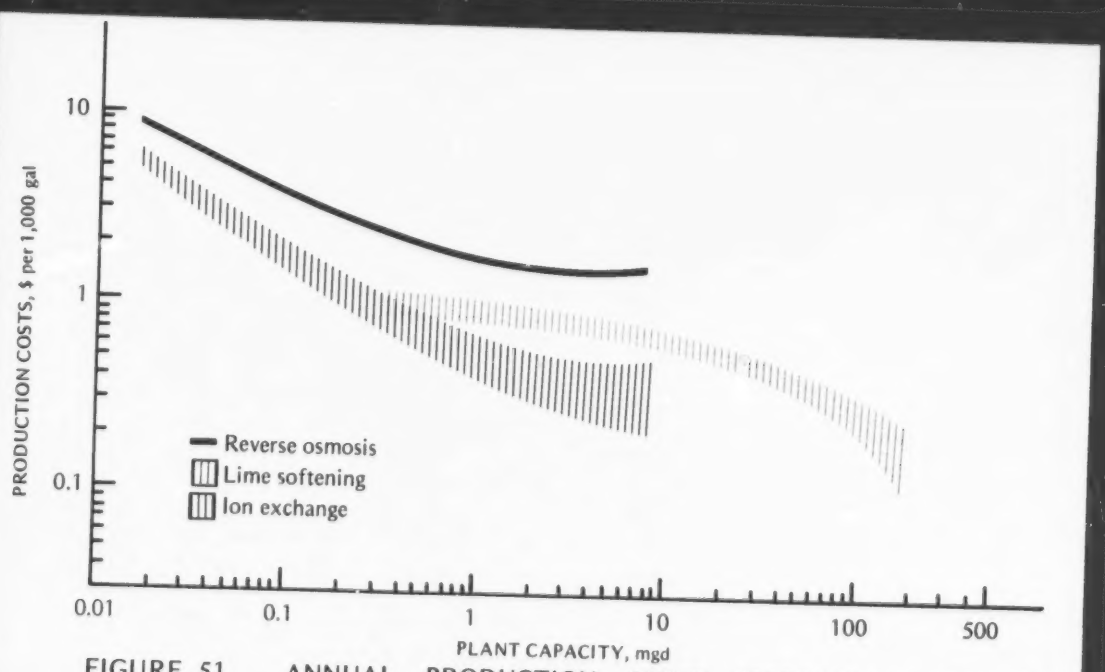


FIGURE 51 ANNUAL PRODUCTION COSTS (OPERATION, MAINTENANCE, AMORTIZATION) FOR 7.5 pCi/l RADIUM-226 IN RAW WATER

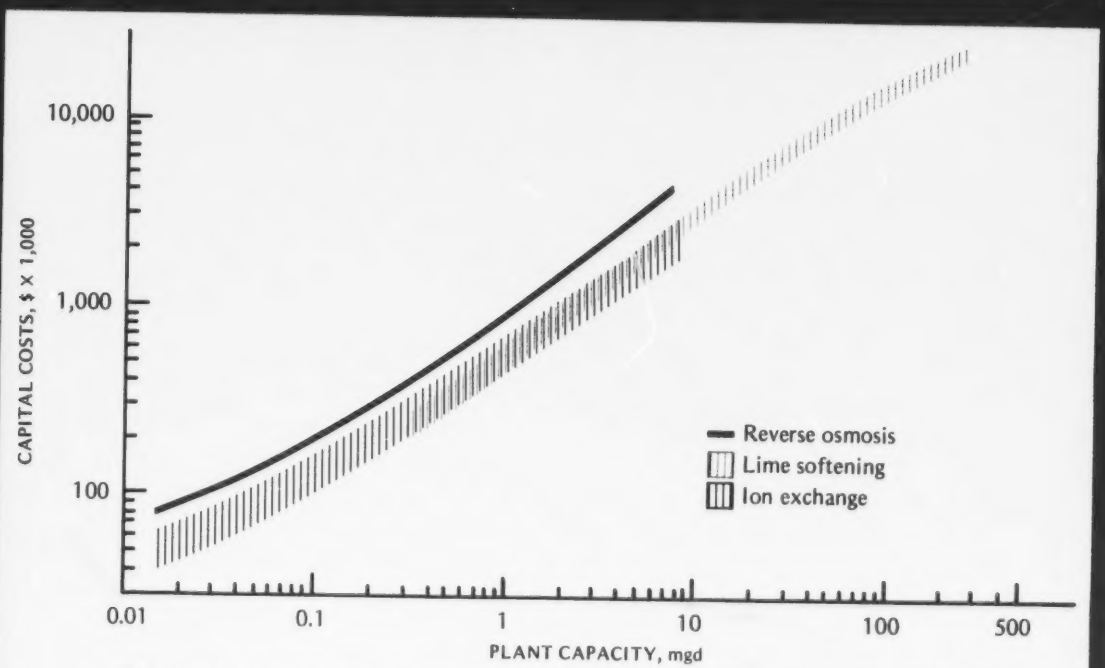


FIGURE 52 CAPITAL COST FOR WATER TREATMENT PLANTS FOR 20 pCi/l RADIUM-226 IN RAW WATER

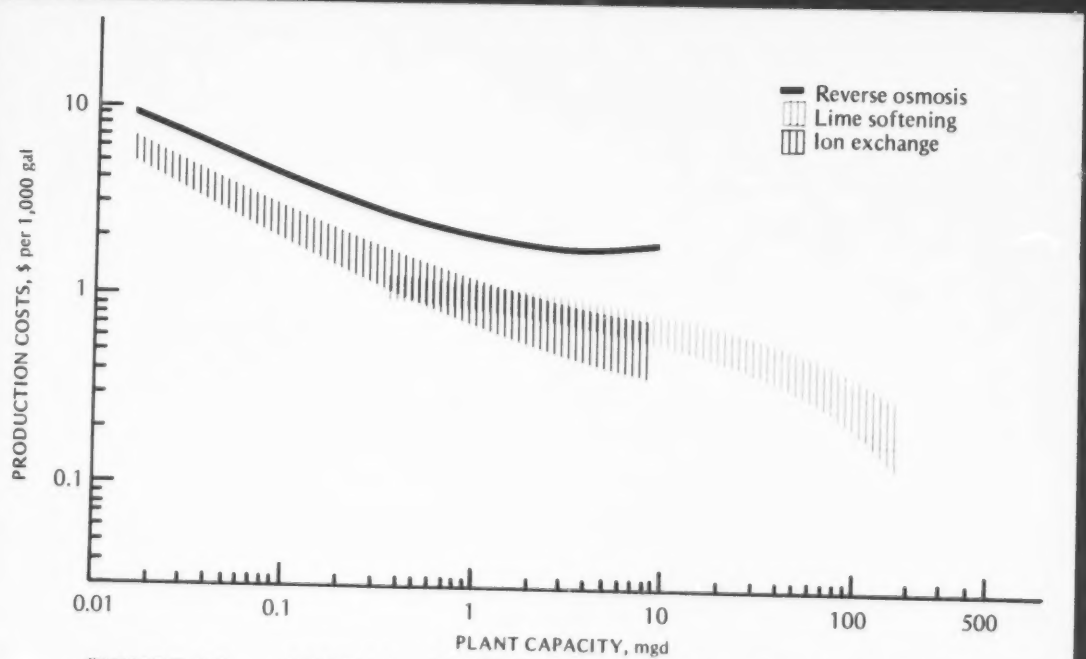


FIGURE 53 ANNUAL PRODUCTION COSTS (OPERATION, MAINTENANCE, AMORTIZATION) FOR 20 pCi/l RADIUM-226 IN RAW WATER

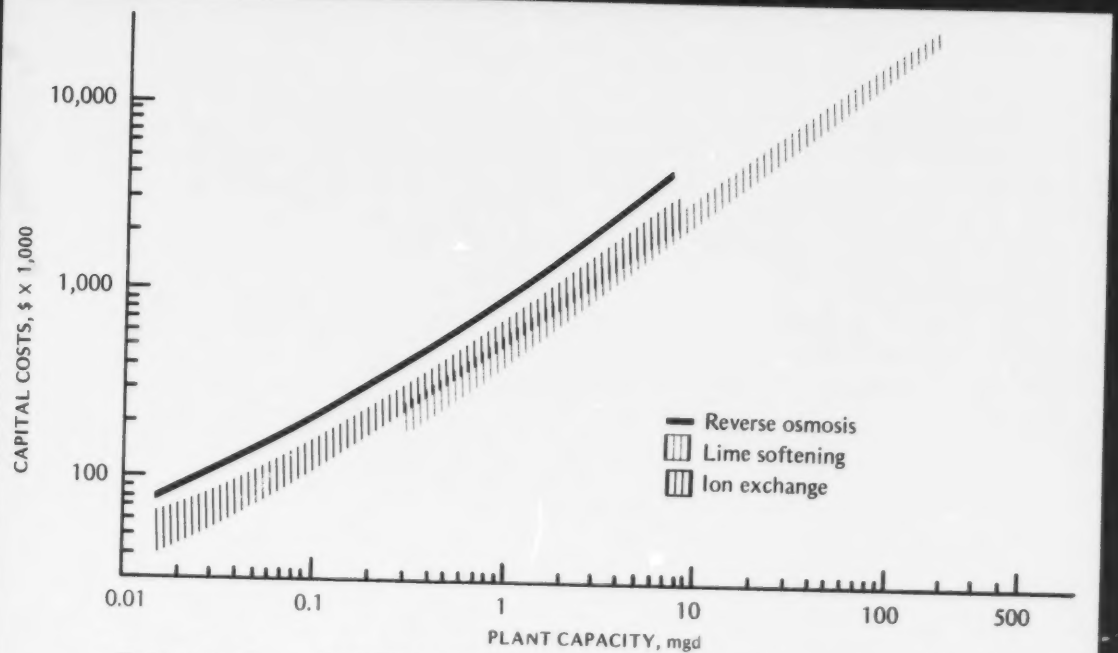


FIGURE 54 CAPITAL COST FOR WATER TREATMENT PLANTS FOR 50 pCi/l RADIUM-226 IN RAW WATER

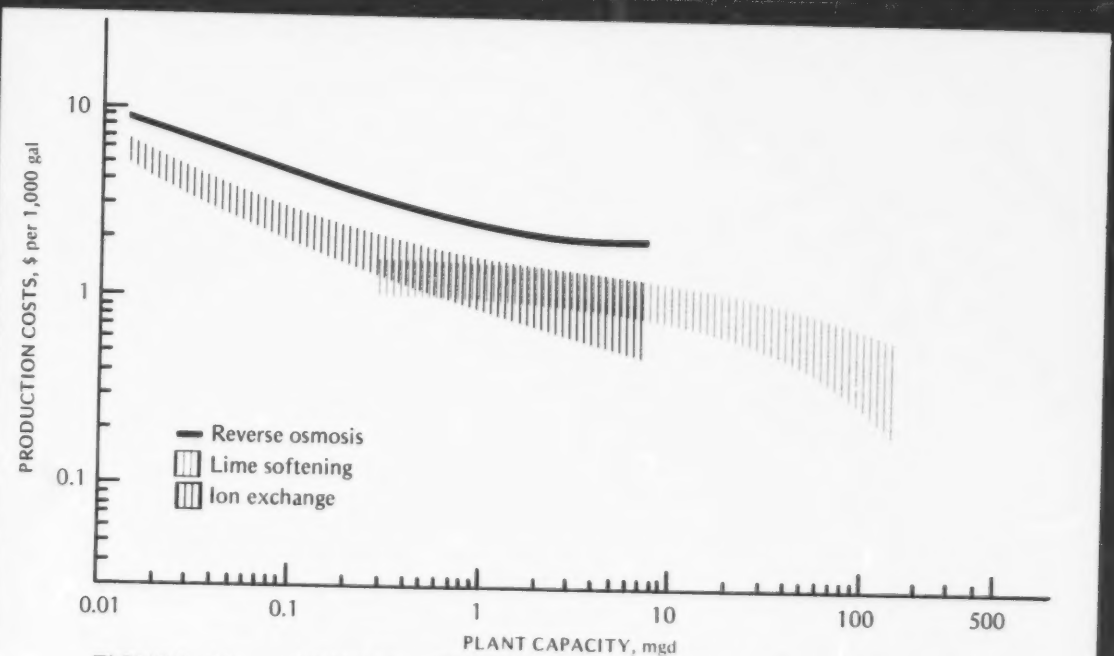


FIGURE 55 ANNUAL PRODUCTION COSTS (OPERATION, MAINTENANCE, AMORTIZATION) FOR 50 pCi/l RADIUM-226 IN RAW WATER

dation of existing waters rather than to bring about a massive cleanup program. The Interim Drinking Water Regulations (13) stated:

> The 4 millirem per year standard for man-made radioactivity was chosen on the basis of avoiding undesirable future contamination of public water supplies as a result of controllable human activities. Given current levels of fallout radioactivity in public water supply systems and their expected future declines and the degree of control on effluents from the nuclear industry that will be exercised by regulatory authorities, it is not anticipated that the maximum contaminant levels for man-made radioactivity will be exceeded except in extraordinary circumstances.

MONITORING FOR BETA AND PHOTON EMITTERS

Monitoring requirements for manmade radiation are stated in the Drinking Water Regulations, in part, as:

> (1) Within two years of the effective date of this part, systems using surface water sources and serving more than 100,000 persons and such other community water systems as are designated by the State shall be monitored for compliance . . .

Required monitoring is limited to systems serving more than 100,000 persons and using surface water, because EPA felt that these systems would be more likely to have manmade radioactive contamination. Small supplies are not required to be monitored because of analytical costs and the number of laboratories available to do the radiochemical analyses.

REMOVAL OF MANMADE RADIOACTIVITY

Because the beta and photon radiation limit is not expected to be exceeded, detailed treatment guidelines are not necessary. However, certain fundamentals should be set forth. It is the purpose of this guideline to discuss only the basic concepts of radioisotope removal.

If a drinking water has gross beta activity exceeding 50 pCi/l, Interim Drinking Water Regulations require that an analysis be performed to determine the major radioactive constituents present. The regulations also require that organ and body doses be calculated. If the 4-mrem/yr dose limit is exceeded, treatment for removal of a portion of the radioactivity would be required.

Although it would be necessary to remove a radioisotope because of its radioactive properties, the actual removal technique should be related to the chemical properties of the radionuclide. In water treatment processes, radioactive substances, such as strontium-90, behave the same as the nonradioactive, or stable, element. Thus, treatment techniques cannot be given for beta emitters or gamma emitters as a class, but each radioisotope must be considered separately when it is found in water.

Data on removal of a number of specific radionuclides and on fission product mixtures have been summarized by Straub (14). The most effective conventional water treatment techniques were lime softening and ion exchange softening. Excess lime softening followed by filtration achieved strontium removals of 87-96 percent. Ion exchange with greensand gave 75 percent removal for yttrium-91 and 96+ percent removal of scandium-46, strontium-89, and a barium-140-lanthanum-140 mixture.

Other data indicate that reverse osmosis should be effective for removing radioactivity when the contaminants are in a dissolved ionic form. Hauck and Sourirajan reported 96.5 percent removal for strontium chloride fed at 485 mg/l (15). In a discussion of heavy metals removal tests with 500 mg/l of solutes, the authors stated that "the same degree of separation can be expected at lower concentrations . . ."

The ability of reverse osmosis to remove very dilute ions from solution was demonstrated in the data on radium removal given earlier. The quantities of radium in the raw or feed water were in the picogram range, yet reverse osmosis gave radium removals of greater than 90 percent.

Investigations have shown that heavy metals (Cd, Cr, Cu, Zn), barium, and cesium can be removed by reverse osmosis. Mixon (16) demonstrated removals of 90 percent and more for Ba, Cd, Cr, Cu, and Zn. Lonsdale et al. (17) reported removals of 98 percent or more for cesium chloride and strontium chloride.

Studies by Russian investigators (18) showed reverse osmosis to be effective for treating low level wastes. A model wastewater containing $NaNO_3$ in amounts from 0.5-32 g/l was spiked with beta radioactivity (0.1-100 μCi/l) by adding iodine-131, cerium-144, cesium-137, zirconium-95, strontium-83, or cobalt-60. The authors reported 90 percent removals. Unpublished data show 95 percent or better removal of cesium-134, cesium-137, and cobalt-60 by reverse osmosis when these nuclides were present in

the feed water in the microcurie-per-liter concentration range. Treatment of a low-level radioactive laundry waste by reverse osmosis resulted in removal of more than 99 percent of the radioactivity (19).

Reverse osmosis appears to be a very promising way to remove most of the multitude of possible beta and photon emitters. Good engineering practice, however, would be to perform pilot-scale tests with a small reverse osmosis unit before installing a full-scale treatment plant.

Costs for removal of beta and photon emitters were not given by the authors. For a preliminary estimate of costs, the radium removal costs given for lime softening, ion exchange, and reverse osmosis should suffice.

Glossary

Dose equivalent. The product of the absorbed dose from ionizing radiation and such factors as account for differences in biological effectiveness caused by the type of radiation and its distribution in the body as specified by the International Commission on Radiological Units and Measurements.

Gross alpha particle activity. The total radioactivity resulting from alpha particle emission as inferred from measurements on a dry sample.

Gross beta particle activity. The total radioactivity resulting from beta particle emission as inferred from measurements on a dry sample.

Manmade beta particle and photon emitters. All radionuclides emitting beta particles and/or photons listed in NBS Handbook 69 (12), except the daughter products of thorium-232, uranium-235, and uranium-238.

Picocurie (pCi). That quantity of radioactive material producing 2.22 nuclear transformations per minute.

Quality factor (QF). Related to the potential a type of radiation has for causing biological damage. QF is related to the energy deposited by radiation per unit distance in absorbing tissue. It is more harmful biologically to deposit a unit of energy in a very short distance than to distribute the energy deposi' over a long distance.

Rad. The energy released when ionizing radiation absorbed is measured in rads, the radiation absorbed dose. The rad is defined as the dose of any ionizing radiation that is accompanied by the liberation of 100 ergs of energy per gram of absorbing material.

Rem. The unit of dose equivalent from ionizing radiation to the total body or any internal organ or organ system. A millirem (mrem) is 1/1000 of a rem. Rem was also defined and explained by Glasstone (20) as, "1 rem is taken to be the quantity of radiation which produces the same biological damage in man as that resulting from the absorption of 1 rad of X-rays or gamma rays."

References

1. National Primary Drinking Water Regulations. *Fed. Reg.*, July 9, 1976.
2. *Basic Radiation Protection Criteria.* NCRP Report No. 39. National Council on Radiation Protection and Measurements, Bethesda, Md., 1971.
3. Hursh, John B. Radium Content of Public Water Supplies. *J. Am. Water Works Assoc., 63*(Jan.), 1954.
4. *Statement of Basis and Purpose for the Proposed National Interim Primary Drinking Water Regulations, Radioactivity.* U.S. Environmental Protection Agency, Washington, D.C., Aug. 15, 1975. Pp. 64-67.
5. Determination of Radium Removal Efficiencies in Illinois Water Supply Treatment Processes. Technical Note ORP/TAD-76-2, U.S. Environmental Protection Agency, Washington, D.C., May 1976.
6. Determination of Radium Removal Efficiencies in Iowa Water Supply Treatment Processes. Technical Note ORP/TAD-76-1, U.S. Environmental Protection Agency, Washington, D.C., June 1976.
7. Singley, J. E., et al. *Costs of Radium Removal from Potable Water Supplies.* EPA-600/2-77-073. U.S. Environmental Protection Agency, Cincinnati, Ohio, 1977. In press.
8. Unpublished data, U.S. Environmental Protection Agency, Water Supply Research Division, MERL, Cincinnati, Ohio.
9. Sarasota County Health Department news release, Oct. 26, 1975.
10. Moore, D. H. Greenfield, Iowa, Reverse Osmosis Plant, *J. Am. Water Works Assoc., 64*(Nov.):781, 1972.

11. *Monograph of the Effectiveness and Cost of Water Treatment Processes for the Removal of Specific Contaminants.* Vol. 1. *Technical Manual.* Prepared for the EPA Office of Air and Water Programs by David Volkert and Associates, Aug. 1974.
12. *Maximum Permissible Body Burdens and Maximum Permissible Concentration of Radionuclides in Air or Water for Occupational Exposure.* NBS Handbook No. 69, U.S. Department of Commerce, Washington, D.C., Aug. 1963.
13. National Primary Interim Drinking Water Regulations. *Fed. Reg.*, Aug. 14, 1975.
14. Straub, C. P. Removal of Radioactivity by Water-Treatment Processes. In: *Low Level Radioactive Wastes—Treatment, Handling, Disposal.* U.S. Atomic Energy Commission, Washington, D.C., 1964. Ch. 8.
15. Hauck, A. R., and S. Sourirajan. Performance of Porous Gellulose Acetate Membranes for the Reverse Osmosis Treatment of Hard and Waste Waters. *Environ. Sci. Technol.*, *3*(Dec.): 1272-1274, 1969.
16. Mixon, F. O. The Removal of Toxic Metals from Water by Reverse Osmosis. Office of Saline Water Report 73-889, Sept. 1973. Pp. 3-5.
17. Lonsdale, H. K., et al. Research on Improved Reverse Osmosis Membranes. Office of Saline Water Report No. 577, Oct. 1970. P. 110.
18. Dytnerskii, Y. F., et al. Purification and Concentration of Liquid Wastes with a Low Level of Radioactivity by Reverse Osmosis. *At. Energy*, *35*(6):405-408, 1973. Cited in: *Chem. Abstr.*, *81*:130, 1974.
19. Koenst, J. W., et al. The Treatment of PWR Nuclear Process Wastes Using Membrane Systems. In: *Proceedings of the 28th Industrial Waste Conference.* Purdue University, Lafayette, Indiana, May 1-3, 1973. P. 765.
20. Glasstone, S. *Sourcebook on Atomic Energy*, D. Van Nostrand and Company, Inc., New York, N.Y., 1967. P. 741.